

13th International Conference on Environmental Catalysis

Isola delle Femmine (PA - Sicily), Italy

2-5 June 2025

BOOK OF ABSTRACTS

Editors

- Prof. Gabriele Centi, ERIC a.i.s.b.l.
- Prof. Enrico Tronconi, Politecnico Milano
- Prof.sa Siglinda Perathoner, Univ. Messina

Published by

European Research Institute of Catalysis (ERIC aisbl), Brussels (Belgium)

Copyright ERIC aisbl, reproduction not allowed except for personal use.

First Edition

© 2025 Brussels, Belgium by ERIC aisbl Press

https://www.eric-aisbl.eu/

725 pages

Original Title

Book of Abstract. 13th International Conference on Environmental Catalysis (ICEC 2025)

Graphic design and layout

ERIC aisbl Press

ISBN

ISBN 979-12-210-9763-4



Preface

The 13th International Conference on Environmental Catalysis (ICEC2025) has been held on June 2-5 (Monday-Thursday), 2025 at "SARACEN SANDS HOTEL & CONGRESS CENTRE" in Isola delle Femmine (Palermo, Sicily - Italy). The conference follows ICEC2022, which was held at Kansai University in Osaka, Japan, from July 30 to August 2, 2022. The conference is the major event in environmental catalysis.

After three decades, in a deep transition period to a new low-carbon economy, ICEC returns to Italy to discuss the future of environmental catalysis. The conference sub-title was "Addressing the new challenges", because it aims to redefine the fundamental and applied research on environmental catalysis to address the 2050 challenges.

The congress is organised by ERIC aisbl (European Research Institute of Catalysis) in collaboration with the Italian Group of Catalysis (GIC) and the Division of Industrial Chemistry of the Italian Chemical Society (SCI), and the contribution of the University of Messina (Italy), Politecnico Milano (Italy) and Forschungszentrum Jülich GmbH (Germany).

Conference Theme

Fundamental and applied research on environmental catalysis and catalysts to address the 2050 challenges (a resilient and zero-carbon society). Topics include, but were not limited to:

- Automotive and stationary emission control
- Air cleaning and combustion
- Water treatment
- Sustainable and clean energy production and transport
- Catalysis to electrify the chemical production
- Green chemistry and biomass transformation, renewable resources conversion
- Circular economy
- CO2 utilisation and recycling
- H2 storage and transportation, green H2 production, hydrogen vectors
- Photocatalysis and photoelectrocatalytic approaches, solar energy utilisation
- Advanced process with electrocatalysis and plasma utilisation
- Fundamental advances in understanding catalysis
- Multiscale modelling and advanced simulation aspects

More than 400 participants from 40 countries attended the congress, which was organised over four intense days, featuring three parallel sessions and nearly 300 communications, including plenary and keynote talks, oral and short oral presentations, and two poster sessions.

ICEC 2025 was a paperless congress that respected the principles of sustainability and promoted cross-fertilisation in various areas of environmental catalysis.

Chairs

- Prof. Gabriele Centi, ERIC a.i.s.b.l.
- Prof. Enrico Tronconi, Politecnico Milano
- Prof.sa Siglinda Perathoner, Univ. Messina

Programme Committee

L. Lietti (Chair, PoliMI), P. Fornasiero (co-chair, UniTS), A. Agostiano (UniBA), A. Aricò (CNR ITAE), S. Albonetti (UniBO), F. Basile (UniBO), P. Barbaro (ICCOM-CNR), S. Bensaid (PoliTO), F. Bella (PoliTO), M. Bonchio (UniPD), S. Bordiga (UniTO), G. Busca (UniGE), .C Cannilla (CNR ITAE), F. Cavani (UniBO), P. Ciambelli (UniSA), V. Conte (UniRM), L. Curri (UniBA), C. De Leitenburg (UniUD), D. Fino (PoliTO), G. Giambastiani (UNIFI-DICUS), G. Giordano (UniCAL), G. Groppi (PoliMi), E. Groppo (UniTO), M. Marchionna (Saipem), S. Gross (UniPD), M. Guidotto (CNR ISTM), S. Hernandez (PoliTO), F. Mauriello (UniRC), M. Migliori (UniCAL), R. Millini (Eni), I. Nova (PoliMI), R. Pirrone (PoliTO), R. Psaro (CNR ISTM), A.M. Raspolli Galletti (UniPI), S.Scirè (UniCT), M. Di Serio (UniNA), M. Signoretto (UniVE), A. Trovarelli (UniUD)

Organising and Local Committees

C. Ampelli (Chair, UniME), A. Beretta (co-chair, PoliMI), T. Merdzhanova (co-chair, Jülich), S. Abate (UniME), G. Bonura (CNR ITAE), A.M. Casella (ERIC), D. Di Vivona (ERIC), C. Genovese (UniME), G. Giorgianni (UniME), C. Italiano (CNR, ITAE), P. Lanzafame (UniME), F. Liotta (CNR ISMN), M. Maestri (PoliMI), G. Papanikolaou (UniME), R. Passalacqua (UniME), F. Tavella (UniME), S. Vannuzzi (ERIC), C.G. Visconti (PoliMI)

International Advisory Board

ICEC International Advisory Board, all Board Members, chaired by M. Stockenhuber (Australia), integrated by renowned scientists in the field: R. Arrigo (Salford Univ., UK), A. Bogaerts (Antwerp Univ, Belgium), A. Dibenedetto (University of Bari, Italy), V. Hessel (Adelaide Univ, Australia), J. Lercher (PNNL, US), G. Marin (Gent Univ, Belgium), I.-S. Nam (Pohang Uni S&T, Korea), V.I. Parvulescu (Univ. Bucharest, Romania), J. Pérez-Ramírez (ETH Zurich, Switzerland), J. Ramon Galan (ICIQ, Spain), E. Rebrov (Univ. Warwick, UK), A. Quadrelli (Lyon, France), B. Weckhuysen (Utrecht Univ., The Netherlands), T. Zhang (DICP, China)

Organizing Institutions and Sponsors

ORGANIZERS

PLATINUM SPONSORS

Projects sponsoring ICEC 2025

Sponsoring prizes and lecture

Grants for early stage researchers

Exhibitors

	2025	2/6 MON			3/6 TUE			4/6 WED			5/6 THU		
	Room	PR			PR			PR			PR		
	Chair	E. Tronconi			T. Maschmeyer			M. Stockenhuber			A. Corma		
8:50	9:10	Opening (Centi, Perathoner, Tronconi)			PL1 - Yamashita			PL2 - Deutschmann			KP2 - Bogaerts Chemistry Europe Lecturer		
9:10	9:30	KP1 - Biasi											
	9:50												
9:30	9:50										PR	RM	RI
	Room	PR	RM	RI	PR	RM	RI	PR	RM	RI	PR4A	RM4A	RI4A
	Chair	PR1A	RM1A	RI1A	PR2A	RM2A	RI2A	PR3A	RM3A	RI3A	OR91	OR101	OR111
10:00	10:20	OR1	OR10	OR19	OR28	OR37	OR46	OR55	OR67	OR79	OR92	OR102	OR112
10:20	10:40	KN1 Busca	OR11	OR20	OR29	OR38	OR47	OR56	KN8 Villamaina	OR80	OR93	KN4 Canivet	OR113
10:40	11:00		OR12	OR21	OR30	OR39	OR48	OR57		OR81	OR94		OR114
coffee break													
11:20	11:40	OR2	OR13	OR22	OR31	OR40	KN6 Liu	KN7 Vajda	OR68	OR82	SO 91-94	SO 105-108	SO 119-122
11:40	12:00	OR3	OR14	KN3 Lemonidou	OR32	OR41			OR69	OR83			
12:00	12:20	OR4	OR15		OR33	OR42	OR49	OR58	OR70	OR84	OR123	OR103	OR115
12:20	12:30	SO 1-4	SO 11-14	SO 24	SO 31-34	SO 41-44	SO 51-54	OR59	OR71	KN9 Adamski	OR124	OR104	OR116
12:30	12:40							OR60	OR72				
12:40	13:00					meeting ICEC BOARD					OR95	OR105	OR117
lunch break							Intro						
14:55	15:00												
	Chair	PR1B	RM1B	RI1B	PR2B	RM2B	Beretta	PR3B	RM3B	RI3B	PR4B	RM4B	RI4B
15:00	15:20	OR5	KN2 Kim	OR23	OR34	KN5 Daturi	OR50	SO 61-64	SO 71-74	SO 81-84	SO 95-104	SO 109-118	OR125
15:20	15:40	OR6		OR24	OR35		OR51						SO 126-132
15:40	16:00	OR7	OR16	OR25	OR36	OR43	OR52	OR61	OR73	OR85			
16:00	16:20	OR8	OR17	OR26	KN10 Salmi	OR44	OR53	OR62	OR74	OR86			
16:20	16:40	OR9	OR18	OR27		OR45	OR54	OR63	OR75	OR87			

coffee break

	Chair	PR1C	RM1C	RI1C	PR2C	RM2C	RI2C	PR3C	RM3C	RI3C	PR4C	RM4C	RI4C
17:00	17:20	SO 5-10	SO 15-20	SO 25-30	SO 35-40	SO 45-50	SO 55-60	OR64	OR76	OR88	OR96	OR106	OR118
17:20	17:40							OR65	OR77	OR89	OR97	OR107	OR119
17:40	18:00							OR66	OR78	OR90	OR98	OR108	OR120
18:00	18:20	**CH - P1** (40 poster)		# ERC, SUN4Fuel, SCOPE, GreenSwap	**CH** - P2 (42 poster)		Special lecture (30 min)	SO 65-70	SO 75-80	SO 85-90	OR99	OR109	OR121
18:20	18:40										OR100	OR110	OR122
18:40	19:00						§ exhib. (2x15min)				SO133-136	SO137-140	SO141-144
19:00	19:20	# ERC and projects sessions			P. Forzatti session (A. Beretta)						**closing**		
19:20	19:30				§ exhibitors session								
19:30	21:00	Welcome Party			Sicilian Street Food Party						Banquet 20:15-23:00		
21:00	22:30												

Chairs

PR1A	S.Gross	PR2A	J.R. Galan Mascaros	PR3A	M. Guidotti	PR4A	E. Palomares
PR1B	M. Migliori	PR2B	L. Curri	PR3B	C.G. Visconti	PR4B	L. Lisi
PR1C	R. Psaro	PR2C	C. Genovese	PR3C	C. Ampelli	PR4C	S. Abate
RM1A	K. Barbera	RM2A	A.M. Raspolli Galletti	RM3A	M. Maestri	RM4A	S. Hernàndez
RM1B	Y. Li	RM2B	F. Bella	RM3B	G. Giambastiani	RM4B	L.F. Liotta
RM1C	M. Signoretto	RM2C	M. Di Serio	RM3C	E. Groppo	RM4C	P. Lanzafame
RI1A	J. Hargreaves	RI2A	L. Prati	RI3A	F. Di Renzo	RI4A	A. Comotti
RI1B	S. Albonetti	Forzatti	A. Beretta	RI3B	C. Italiano	RI4B	G. Giordano
RI1C	C. Cannilla	RI2C	C. Menegazzo	RI3C	E. Paone	RI4C	R. Passalacqua

Summary

02/06/2025 9

Room PR - Plenary 9
Room Massimo (RM) 12
Room Isola - RI 15

03/06/2025 18

Room PR - Plenary 18
Room Massimo (RM) 22
Room Isole (RI) 25

04/06/2025 29

Room PR - Plenary 29
Room Massimo - RM 32
Room ISOLA - RI 36

05/06/2025 39

Room PR - Plenary 39
Room Massimo - RM 44
Room Isola - RI 48

P1 - POSTER SESSION 1 - 02/06/2025 53

P2 - POSTER SESSION 2 – 03/06/2025 58

PLENARY and KEYNOTE ABSTRACTS (PL1-2, KP1-2, KN1-10) 64

ORAL ABSTRACTS (OR1-124) 90

SHORT ORAL ABSTRACTS (SO1-124) 333

POSTER ABSTRACTS (P1-1-40; P2-1-43) 588

02/06/2025		
Room PR - Plenary		
08:50 - 09:10		Opening (Gabriele Centi, Siglinda Perathoner, Enrico Tronconi)
09:10 – 09:50	KP1	Pierdomenico Biasi CASALE S.A., Lugano, (Switzerland) *Environmental Catalysis in Industry: The Road Ahead* Pierdomenico BIASI, Raffaele OSTUNI, Alberto GARBUJO, Filippo BUTTIGNOL, Ludovica VILLANTIERI, Michal BIALKOWSKI CASALE SA, R&D Division, Via Giulio Pocobelli 6, 6900, Lugano, Switzerland.
10:00 – 10:20	OR1 moved to OR101	Pascal Granger - University of Lille, UCCS CNRS, Lille (France) *Natural Gas Vehicle post-combustion catalysts: How to manage support effect to magnify the performances of noble metals in methane abatement* Amaury Decoster, Fabien Dhainaut, Pascal Granger Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, F-59000 Lille, France
10:20 – 11:00	KN1	Guido Busca (Università di Genova), Genova (Italy) *Zeolite catalysis for (bio)ethanol-to-hydrocarbons processes* Guido Busca, Elena Spennati, Paola Riani, Gabriella Garbarino - University of Genova, DICCA, via Opera Pia 15, Genova, Italy. - University of Genova, DCCI, via Dodecaneso 31, Genova, Italy.
11:00 – 11:20	Coffee-Break	
11:20 – 11:40	OR2	Henrik Gronbeck - Chalmers University of Technology, Gothenburg (Sweden) *NH_3-SCR over Cu-CHA from first principles* Henrik Grönbeck Competence Centre for Catalysis and Department of Physics, Chalmers University of Technology, Göteborg, Sweden
11:40 – 12:00	OR3	Piotr Pietrzyk Jagiellonian University, Krakow (Poland) *Oxidative half-cycle of SCR NOx on single and dual copper sites of CuSSZ-13 catalyst via NO_2, nitrates and nitrites formation – spectroscopic and thermodynamic DFT background for reaction networks* Bartosz Mozgawa, Filip Zasada, Monika Fedyna, Kinga Góra-Marek, Zbigniew Sojka, Piotr Pietrzyk Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, Krakow, Poland.
12:00 – 12:20	OR4	Elisabetta Finocchio - (Università di Genova), Genova (Italy) *Ternary Me–P–Si oxides for catalytic conversion of biomass-derived chemicals: a closer look at the surface.* Elisabetta Finocchio, Antonella Gervasini, Sebastiano Campisi, Aurelio Bifulco, Claudio Imparato, Antonio Aronne. 1 Università di Genova, Dip. Ingegneria Civile, Chimica e Ambientale, Via Opera Pia 15, Genova, Italy. 2 Università di Milano, Dip. Chimica, Via Camillo Golgi 19, Milano, Italy. 3 Università di Napoli Federico II, Dip. Ingegneria Chimica, dei Materiali e della Produzione Industriale, P.le Tecchio 80, Napoli, Italy.
		Short Orals
12:20 – 12:30	SO1	Gabriella Garbarino – University of Genova, DICCA Dept., Genova (Italy) *Transition metals over C-based materials: unraveling performances and challenges* Sina E. Atakoohi1, Elena Spennati1,2, Paola Riani2,3, Gabriella Garbarino1,2, 1 University of Genova, DICCA Dept., Genova, 16145 (Italy) 2 INSTM, UDR Genova, 16146 (Italy) 3 University of Genova, DCCI Dept., Genova, 16146 (Italy)
12:30 – 12:40	SO2	Michele Leone – Università La Sapienza, Roma (Italy) *Operando-FTIR investigation of bifunctional Pt or Pd,Fe-HMOR catalyst for simultaneous abatement of NOx and N_2O by CH_4* Michele Leone1, Chiara Caponera1, Daniela Pietrogiacomi1, Simone Morpurgo1, Maria Cristina Campa2 1Chemistry Department, Sapienza University of Rome, 00185 Rome, Italy.

		2 ISMN-CNR, c/o Chemistry Department, Sapienza University of Rome, 00185 Rome, Italy.
12:40 – 12:50	SO3	Florian Maurer - Karlsruhe Institute of Technology, Karlsruhe (Germany) *Descriptors for noble metal redispersion on CeO_2-based catalysts* Florian Maurer1, Agustin Salcedo2, Maria Casapu1, David Loffreda2, Arik Beck1, Paolo Dolcet3, Mimoun Aouine4, Thierry Epicier4, Stéphane Loridant4, Philippe Vernoux4, Carine Michel2, Jan-Dierk Grunwaldt1 1 Institute of Chemical Technology and Polymer Chemistry, KIT, Karlsruhe, Germany 2 ENSL, CNRS, Laboratoire de Chimie, Lyon, France 3 Department of Chemical Sciences, University of Padova, Padova 35131, Italy
12:50 – 13:00	SO4	Valérie Meille - *University of Lyon*, IRCELYON, CNRS, Villeurbanne (France) *In-situ DRIFTS studies provide insight into competitive adsorption of VOCs and ozone on catalyst surfaces at low temperature* Amira Jabbari-Hichri1, Salma Majdoub1, Eddy J. Moreno1, Xiaolong Ji1, Valérie Meille1, Sonia Gil1 *IRCELYON, University of Lyon, CNRS, Lyon, 69626 Villeurbanne Cedex, France*
13:00 – 15:00	Lunch Break	
15:00 – 15:20	OR5	Filippo Buttignol - Casale SA, Dipartimento di Ricerca di Base, Lugano (Switzerland) *Iron-catalyzed cooperative red-ox mechanism for the simultaneous conversion of nitrous oxide and nitric oxide* Filippo Buttignol12, Jörg W. A. Fischer3, Alberto Garbujo4,, Pierdomenico Biasi4, Gunnar Jeschke5, Oliver Kröcher1,2 and Davide Ferri1 1 Paul Scherrer Institut (PSI), Center for Energy and Environmental Sciences, 5232 Villigen, Switzerland. 2 École Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland. 3 ETH Zurich, Laboratory of Physical Chemistry, 8093 Zurich, Switzerland
15:20 – 15:40	OR6	Sang Woo Byun - Gwangju Institute of Science and Technology, Gwangju South Korea *Upcycling degraded Li(Ni-Co-Mn)O_2 cathodes to highly active thermal catalyst via the lithium pre-extraction method for air pollutant abatement* Sang Woo Byun1, Hyeonwoo Shin1, Wonseok Choi1, Jinju Song2, Dokyeong Han2, Jiyoung Ma2, Jayoung Kim2, Seok Hyun Song2, Jung-Je Woo2 and Sung Bong Kang, 1 1 Gwangju Institute of Science and Technology, 123 Cheomdan-Gwagiro, Gwangju 61005, South Korea 2 Gwangju Clean Energy Research Center, Korea Institute of Energy Research (KIER), Gwangju 61003, South Korea
15:40 – 16:00	OR7	Fabien Can - IC2MP, Université de Poitiers-CNRS, Poitiers (France) *H_2-SCR over 0.3%Pt/5%SiO_2-Al_2O_3 catalyst: investigations in the reaction pathways* Amira Ben Attia1, Fabien Can1, Xavier Courtois1 1 IC2MP, Université de Poitiers-CNRS, 4 rue Michel Brunet TSA 51106 86073 Poitiers Cedex 9, France.
16:00 – 16:20	OR8	Daniel C. Cano-Blanco - Paul Scherrer Institute, Villigen (Switzerland) *Site-specific monomeric Fe sites catalyze the N_2O decomposition reaction* Daniel C. Cano-Blanco1, Jörg W. A. Fischer3, Filippo Buttignol1, Gunnar Jeschke3, Oliver Kröcher1,2, Davide Ferri1 1 Paul Scherrer Institute, 5232 Villigen, Switzerland; 2 Institute for Chemical Science and Chemical Engineering, École polytechnique fédérale de Lausanne (EPFL), Lausanne, Switzerland; 3 Dept. Chemistry and Applied Biosciences, ETH Zurich, 8093 Zurich, Switzerland
16:20 – 16:40	OR9	Maria Casapu - Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology, Karlsruhe (Germany) *Structural parameters for high activity and stability of Pd/CeO_2 CH_4 oxidation catalysts* D. Zengel1, V. Marchuk1, M. Kurt1, F. Maurer1, A. Salcedo2, C. Michel2, D. Loffreda2, M. Aouine3, T. Epicier3, S. Loridant3, P. Vernoux3, M. Casapu1, J.-D. Grunwaldt1 1 Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany 2 ENS de Lyon, CNRS UMR 5182, Laboratoire de Chimie, Lyon, France

		3Institut de Recherches sur la Catalyse et l'Environnement de Lyon, CNRS UMR5256, Université de Lyon, Lyon, France
16:40 – 17:00	Coffee-Break	
		Short Orals
17:00 – 17:10	SO5	Roberta Castiglione – Laboratory of Catalysis and Catalytic Processes. Politecnico di Milano – Milano (Italy) *Anisotropic POCS: Unlocking Mass Transfer Potential* Roberta Castiglione1, Claudio Ferroni1, Federico Sascha Franchi1, Matteo Ambrosetti, Mauro Bracconi, Gianpiero Groppi, Matteo Maestri, Enrico Tronconi Laboratory of Catalysis and Catalytic Processes, Politecnico di Milano, 20156 Milan, Italy
17:10 – 17:20	SO6	Matteo Maestri – Politecnico di Milano, Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Milano (Italy) *H_2O-assisted Oxidation Half-Cycle of Low Temperature NH3-SCR over Cu-CHA* Gabriele Contaldo1, Isabella Nova1, Matteo Maestri1, and Enrico Tronconi1, 1Politecnico di Milano, Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Via la Masa 34, Milano 20156, Italy.
17:20 – 17:30	SO7	Andrea De Giacinto - Karlsruher Institut für Technologie (KIT), Karlsruhe (Germany) *Influence of CeO_2 morphology and initial Pd-Pt interaction degree on catalyst activity and stability* Andrea De Giacinto1,2, Paolo Dolcet1,2, Di Wang3,4, Joachim Czechowsky1, Carina Maliakkal3, Christian Kübel3,4, Silke Behrens5, Jan-Dierk Grunwaldt1,5, Silvia Gross1,2, Maria Casapu1 1 Karlsruhe Institute of Technology, Institute for Chemical Technology and Polymer Chemistry, Engesserstraße 18-20, 76131 Karlsruhe, Germany 2 Università di Padova, Dip Scienze Chimiche, Via Marzolo 1, 35131 Padova, Italy 3 Karlsruhe Institute of Technology, Institute of Nanotechnology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany 4 Karlsruhe Institute of Technology, Karlsruhe Nano Micro Facility, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany 5 Karlsruhe Institute of Technology, Institute of Catalysis Research and Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
17:30 – 17:40	SO8	Jean-Marc Giraudon - Univ. Lille, CNRS, Centrale Lille, Univ. Artois, Unité de Catalyse et Chimie du Solide, Lille (France) *Functionalization of hydroxyapatite with silver for application in total oxidation of formaldehyde* E. Prandini1,2, G. Abdallah1, S. Campisi2, A. Gervasini2, A. Addad3, O. Gardoll1, M. Trentesaux1, J.-M. Giraudon1, J.-F. Lamonier1 1 Univ. Lille, CNRS, Centrale Lille, Univ. Artois, Unité de Catalyse et Chimie du Solide-Lille, 59000, France. 2 Dipartimento di Chimica, Università degli Studi di Milano, Via C. Golgi 19, Milano, 20133, Italy. 3 Univ. Lille, CNRS, INRAE, Centrale Lille, Unité de Matériaux et Transformations-Lille, 59000, France
17:40 – 17:50	SO9	Vincenzo Russo, University of Naples Federico II, Naple (Italy) *LOHC: kinetics of toluene hydrogenation over Pt/Al_2O_3 catalyst in a trickle bed reactor* Vincenzo RUSSO,1, Muhammad Usama DAUD1, Alessandro ESPOSITO1, Federica COSENZA1, Riccardo TESSER1, Martino DI SERIO1 Università di Napoli 'Federico II', Department of Chemical Sciences, Napoli, Italy.
17:50 – 18:00	SO10	Withdrawn
18:00 – 19:00	CH P1	Poster session (Hallway) P1

02/06/2025		
Room Massimo (RM)		
10:00 – 10:20	OR10	Federico Bella – Dept.Applied Science and Techn., Politecnico di Torino, Torino (Italy) *Lithium-mediated pathways towards ammonia electroproduction* Anna Mangini, Sara Garcia-Ballesteros, Federico Bella Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 – Torino, Italy.
10:20 – 10:40	OR72 subst. OR11	Enrico Tronconi – Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, Milan (Italy) *Deconvolving the Standard-SCR Redox Mechanism on Copper-Zeolites for Catalyst Insight and Development* Andrea Gjetja1, Nicola Usberti1, Nicole Daniela Nasello1, Umberto Iacobone1, Isabella Nova1, Enrico Tronconi,1, Roberta Villamaina2, Maria Pia Ruggeri2, Djamela Bounechada2, Andrew P. E. York2, Jillian Collier2 1 Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, Via La Masa, 34, 20156 Milan, Italy 2 Johnson Matthey Technology Centre, Blounts Court Road, Sonning Common, Reading RG4 9NH, UK
10:40 - 11:00	OR12	Sebastián Gámez – Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, Louvain-la-Neuve (Belgium) *Mesoporous Ni/La_2O_3 catalyst for highly efficient NH_3 decomposition* Sebastián GAMEZ1, Josefine SCHNEE2 and Eric M. GAIGNEAUX1 1 Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, Pl. Louis Pasteur 1, 1348 Louvain-la-Neuve, Belgium. 2 Sorbonne Université, Laboratoire de Réactivité de Surface (LRS), CNRS, Campus Pierre et Marie Curie, 4 Place Jussieu, F-75005 Paris Cedex 05, France
11:00 – 11:20	Coffee-Break	
11:20 – 11:40	OR13	Roberto Luigi Oliveri – Dipartimento di Ingegneria, Università di Palermo, Palermo (Italy) *Alkaline electrolyzer with nanostructured NiFeP electrodes for hydrogen production* Roberto Luigi Oliveri,1, Salvatore Geraci1 , Bernardo Patella1 , Giuseppe Aiello1, Sonia Longo1, Alberto Affranchi1, Maurizio Cellura1, Rosalinda Inguanta1 1 Dipartimento di Ingegneria, Università degli Studi di Palermo, 90128 Palermo, Italy 2 Centro di Sostenibilità e Transizione Ecologica
11:40 – 12:00	OR14	Cristina Italiano – CNR-ITAE "Nicola Giordano", Messina (Italy) *Low-temperature CO_2 methanation over Ni-based catalysts: On the nature of active sites by operando DRIFTS study* Cristina Italiano, Gabriel Marino, Minju Thomas, Hafedh Brahim, Miriana Caporlingua, Antonio Vita CNR-ITAE "Nicola Giordano", Via S. Lucia sopra Contesse 5, 98126 Messina, Italy
12:00 – 12:20	OR15	Eleonora La Greca – ISMN-CNR, Palermo (Italy) *Photoreforming of Glycerol for H_2 Production Using Au-Ni Catalysts Supported on CeO_2* Eleonora La Greca1,2, Roberto Fiorenza2, Maria Teresa Armeli Iapichino2 Salvatore Scirè2 and Leonarda Francesca Liotta1 1 Institute for the Study of Nanostructured Materials (ISMN), National Research Council (CNR), Via Ugo La Malfa 153, 90146 Palermo, Italy 2 Department of Chemical Science, University of Catania, Viale A. Doria 6, Catania, Italy
		Short Orals
12:20 – 12:30	SO11	Sabrina Akrour – Sorbonne Université, CNRS, Laboratoire Réactivité de Surface, LRS, Paris (France) *Green NH_3 Synthesis via Hydroxyapatite-Supported Ru Catalysts for Sustainable H2 Storage under mild conditions* Sabrina Akrour1, Alexandre Vimont2, Sandra Casale1, Guylène Costentin1 and Cyril Thomas1

		1Sorbonne Université, CNRS, Laboratoire Réactivité de Surface, LRS, Paris, 75005, France 2Normandie Université, Laboratoire Catalyse et Spectrochimie, 14000 Caen, France
12:30 – 12:40	SO12	Maria Teresa Armeli Iapichino – University of Catania, Department of Chemical Sciences, Catania (Italy) *Solar Photoreforming of biomass and plastic-derived materials using carbon-based photocatalysts* Maria Teresa Armeli Iapichino1, Roberto Fiorenza1, Salvatore Scirè1 University of Catania, Dept. Chemical Sciences, V.le Andrea Doria 6, Catania, Italy
12:40 – 12:50	SO13	Ilaria Barlocco – Dipartimento di Chimica, Università degli Studi di Milano, Milano (Italy) *Probing the Metal/Oxide Interface of IrCoCeOx in $N_2H_4{\cdot}H_2O$ Decomposition: An Experimental and Computational Study* Ilaria Barlocco1, Silvio Bellomi1, Marta Stucchi1, Laura Prati1, Davide Ferri2 and Alberto Villa 1 Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, I-20133 Milano, Italy. 2 PSI Center for Energy and Environmental Sciences, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland
12:50 – 13:00	SO14	Lidia Castoldi, Politecnico di Milano, Milano (Italy) *Iron catalyst for CH_4 pyrolysis: characterizing C formation to understand catalyst deactivation* Lidia Castoldi1, Veronica Piazza1, Chiara Negri1, Marco Orsenigo1, Davide Cafaro1, Matteo Maestri1, Gianpiero Groppi1, Alessandra Beretta,1 1 Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, Via La Masa, 34 – 20156 Milano, Italy.
13:00 – 15:00	Lunch Break	
15:00 – 15:40	KN2	Hyeonjeong Kim – Pohang University of Science and Technology (POSTECH), Division of Environmental Science and Engineering., Pohang (Republic of Korea) *Revisiting Electrochemical Breakpoint Chlorination of Ammonium-Rich Wastewater: Reactive Chlorine Speciation on IrTaOx/TiO_2* Hyeonjeong Kim1 and Kangwoo Cho,1 1 Pohang University of Science and Technology (POSTECH), Division of Environmental Science and Engineering., 77 Cheongam-ro, Pohang, Republic of Korea.
15:40 – 16:00	OR16	Janek Betting – University of Twente, Faculty of Science and Technology, Enschede (The Netherlands) *Detection of Hydroxylamine Intermediate Opens a New Perspective on Ammonia Selectivity in Metal-Catalyzed Nitrate Reduction* Janek Betting, Leon Lefferts, Jimmy Faria Albanese University of Twente, Faculty of Science and Technology, Drienerlolaan 5, 7522NB Enschede, The Netherlands.
16:00 – 16:20	OR17	Antonio Eduardo Palomares - Instituto de Tecnología Química (Universidad Politécnica de Valencia - Consejo Superior Investigaciones Científicas), Valencia (Spain) *Catalytic hydrogenation of chlorated oxyanions in water with Pt-catalysts* Antonio Eduardo Palomares, Adrián Pla-Hernández, Nadia Benmebirouk-Pareja Instituto de Tecnología Química (Universidad Politécnica de Valencia - Consejo Superior Investigaciones Científicas), 46022 Valencia, Spain
16:20 – 16:40	OR18	Pasi Tolvanen – Åbo Akademi, Johan Gadolin Process Chemistry Centre (PCC), Turku/Åbo (Finland) *Catalytic ozonation of pharmaceutical mixtures: A comprehensive analysis of catalyst efficacy, degradation pathways and recyclability* Pasi Tolvanen1, Soudabeh Saeid1, Matilda Kråkström1, Shey Jude Fale1,3, Nikke Saarinen1, Jonna Engström-Öst3, Narendra Kumar, Patrik Eklund1, Jyri-Pekka Mikkola1, Tapio Salmi1,2 1Åbo Akademi, Johan Gadolin Process Chemistry Centre (PCC), FI-20500 Turku/Åbo, Finland

		2Università di Napoli 'Federico II', Chemical Sciences, IT-80125 Napoli, Italy 3 Novia University of Applied Sciences, FI-10650, Finland
16:40 – 17:00	Coffee-Break	
		Short Orals
17:00 – 17:10	SO15	withdrawn
17:10 – 17:20	SO16	Anna Dotti – Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Milano (Italy) *Facile coating of reduced graphene oxide and TiO2 on floating polyurethane foams for photocatalytic water decontamination* Anna Dotti1, Andrea Basso Peressut1, Roberto Matarrese2, Saverio Latorrata1 1Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Piazza Leonardo da Vinci 32, 20133, Milano, Italy. 2Politecnico di Milano, Dipartimento di Energia, Via Lambruschini 4, 20156, Milano, Italy
17:20 – 17:30	SO17	Jiří Henych - Institute of Inorganic Chemistry of the Czech Academy of Sciences, Husinec-Řež (Czechia) *Nanoceria as acid-base catalyst for hydrolysis of sulfonamides, sulfonylureas and other emerging pollutants* Jan Čundrle1, Martin Šťastný1, Jakub Ederer2, Pavel Janoš2, Jiří Henych,1 1Institute of Inorganic Chemistry of the Czech Academy of Sciences, 250 68 Husinec-Řež, Czechia. 2 Jan Evangelista Purkyně University in Ústí nad Labem, Faculty of Environment, Pasteurova 3632/15, 400 96 Ústí nad Labem, Czechia.
17:30 – 17:40	SO18	Elena Mariani – Department of Chemistry, UNIFI, Sesto Fiorentino (Italy) *Efficient palladium recovery and catalyst development from electroplating wastewater using functionalized carbon materials* Elena Mariani1,2,3, Marco Bonechi1,2, Ilaria Maggini1, Claudia Giovani1, Leonardo Lari4,5, Matteo Savastano2,6, Claudio Fontanesi2,7, Antonio Bianchi1, Massimo Innocenti1,2 1 Department of Chemistry, UNIFI, via della Lastruccia 3, 50019 Sesto Fiorentino, Italy. 2 INSTM, via Giuseppe Giusti, 9, 50121 Florence, Italy. 3 Eco-Tech Finish s.r.l., Z.I. San Zeno, Strada C 27, 52100 Arezzo, Italy. 4 School of Physics, Engineering and Technology, University of York, Heslington, York YO10 5DD, UK. 5 The York-JEOL Nanocentre, University of York, Heslington, York YO10 5BR, UK. 6 Department of Human Sciences, University San Raffaele, Via di Val Cannuta 247, 00166 Rome, Italy. 7 Department of Engineering, University of Modena and Reggio Emilia, via Vivarelli 10, 41125 Modena, Italy
17:40 – 17:50	SO19	Channa Najeebullah – Department of Applied Science and Technology, Politecnico di Torino, Torino (Italy) *Bacterial Disinfection from Selected Water Pathogens Using an Iron-doped TiO2 Photocatalyst Under Visible Light* Najeebullah Channa1, Francesca Stefania Freyria1, Tanveer A. Gadhi2, Alessandro Chiadò1, Nicola Blangetti,1 Barbara Bonelli1 1 Department of Applied Science and Technology, Corso Duca degli Abruzzi 24, Politecnico di Torino,10129 Torino, Italy. 2 US-Pakistan Center for Advanced Studies in Water (USPCASW), Mehran University of Engineering and Technology, Jamshoro, 76062, Pakistan.
17:80 – 18:00	SO20	Eleonora Russo – University of Padua, Department of Industrial Engineering, Padova (Italy) *Study on the photodegradation of pharmaceuticals using graphitic carbon nitride derivatives* Eleonora Russo,1, Eryk Fernandes2, João Gomes2, Paolo Sgarbossa1, Rui C. Martins2

		1 University of Padua, Department of Industrial Engineering, via F. Marzolo 9, 35131, Padova, Italy 2 University of Coimbra, Department of Chemical Engineering, rua S. Lima, 3030-790, Coimbra, Portugal
18:00 – 19:00	CH, P1	Poster session (Hallway) - P1

02/06/2025		
Room Isola - RI		
10:00 – 10:20	OR19	Alixandre Magerat – Université catholique de Louvain (UCLouvain), IMCN, Louvain-la-Neuve (Belgium) *Keggin heteropolyanions: novel versatile deoxydehydration catalysts* Alixandre Magerat, Sophie Hermans, Eric M. Gaigneaux Université catholique de Louvain (UCLouvain), Institute of Condensed Matter and Nanosciences (IMCN), Place Louis Pasteur, 1 – 1438 Louvain-la-Neuve, Belgium
10:20 – 10:40	OR37 subs. OR20	Victor Longo – 1University of Messina, Dept. of Chemical, Biological, Pharmaceutical and Environmental Sciences and CASPE INSTM, Messina (Italy) *A new double dielectric barrier discharge (DDBD) reactor to prevent carbon deposition in plasma-assisted non-oxidative methane coupling* Victor Longo, Luana De Pasquale, Siglinda Perathoner, Gabriele Centi, Chiara Genovese University of Messina, Dept. of Chemical, Biological, Pharmaceutical and Environmental Sciences and CASPE INSTM, Viale F.S. D'Alcontres 31, Messina, Italy.
10:40 – 11:00	OR21	Maela Manzoli – University of Turin, Dept. of Drug Science and Technology and NIS, Turin (Italy) *Catalytic synthesis of adipic acid using biomass-derived raw materials* Maela Manzoli1, Fabio Bucciol1, Sara Morandi2, Giancarlo Cravotto1, Svetlana Ivanova3 And Silvia Tabasso1 1University of Turin, Dept. of Drug Science and Technology and NIS Centre, Via P. Giuria 9, 10125, Turin, Italy. 2University of Turin, Dept. of Chemistry and NIS Centre, Via P. Giuria 7, 10125, Turin, Italy. 3University of Seville, Dept. of Inorganic Chemistry, Avda. Americo Vespucio 49, 41092, Seville, Spain
11:00 – 11:20	Coffee-Break	
11:20 – 11:40	OR22	Thomas Maschmeyer - The University of Sydney, Sydney (Australia) *Supercritical Water – Actions and Reactions During the Thermal Decomposition of Plastics* Jack Steel1, Taku Michael Aida2, Anthony F. Masters1, Alexander K.L. Yuen1, Thomas Maschmeyer,1 1The University of Sydney, Laboratory of Advanced Catalysis for Sustainability, School of Chemistry, Sydney NSW 2006, Australia. 2 Fukuoka University, Department of Chemical Engineering, Faculty of Engineering, Nanakuma Jonan-ku, Fukuoka 814-0180, Japan
11:40 – 12:20	KN3	Angeliki Lemonidou – Aristotle University of Thessaloniki, Thessaloniki (Greece) *Upgrading of plastic pyrolysis oil model compounds over ZSM5-based catalysts: Effect of reactor type and operating variables* S-A. Andrianos1, P. Soldatos2, K. Triantafyllidis2, A.A. Lemonidou1 1School of Chemical Engineering, 2School of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece
12:20 – 12:30	SO24	Giulia Forghieri – Università Ca' Foscari Venezia, Via Torino 155, Venezia *Doped-perovskites for the solar-powered photocatalytic valorisation of CO_2* Giulia Forghieri a, Giorgia Ferraro a, Somayeh Taghavi b, Michela Signoretto a a Università Ca' Foscari Venezia, Via Torino 155, Venezia b Faculty of Chemistry, University of Mazandaran, Babolsar 47416-95447, Iran
13:00 – 15:00	Lunch Break	

15:00 – 15:20	OR23	Marina Maddaloni – Department of Civil, Environmental, Architectural Engineering and Mathematics, University of Brescia, Brescia (Italy) *Green Hydrogen from Treated Wastewater via SOECs: A Pathway to Circular Economy and Renewable Energy Integration* Marina Maddaloni1, Matteo Marchionni3, Alessandro Abbá1, Michele Mascia3, Vittorio Tola3, Maria Paola Carpanese4, Giorgio Bertanza1 And Nancy Artioli1 1 Department of Civil, Environmental, Architectural Engineering and Mathematics, University of Brescia, via Branze, 43, 25123 Brescia, Italy 2 Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), University of Brescia, via Branze 38, 25123 Brescia, Italy 3 Department of Mechanical, Chemical and Materials Engineering, University of Cagliari, via Marengo 2, 09123 Cagliari, Italy 4 Department of Civil, Chemical and Environmental Engineering, University of Genova (UNIGEDICCA), via Montallegro 1, 16145 Genoa, Italy
15:20 – 15:40	OR24 (moved to OR97)	Maria Ortega-Jáuregui – Departamento de Ingeniería Química y Bioprocesos, Escuela de Ingeniería, Pontificia Universidad Católica de Chile, Macul, Santiago (Chile) *Ni exsolved nanoparticles from a $La_{1-a}Ni_{1-x}CrxO_3$ perovskite for Methane Steam Reforming* María A. Ortega-Jáuregui1, 2, Deblina Majumder3, Evangelos I. Papaioannou3 Francisco García-García2, Elodie Blanco1, Néstor Escalona1 1 Departamento de Ingeniería Química y Bioprocesos, Escuela de Ingeniería, Pontificia Universidad Católica de Chile, Macul, Santiago, Chile. 2 Institute for Materials and Processes, School of Engineering, University of Edinburgh, Edinburgh, Scotland, United Kingdom. 3 Materials, Concepts & Reaction
15:40 – 16:00	OR25	Ida Ritacco – Dipartimento di Chimica e Biologia, Università degli Studi di Salerno, Fisciano, Salerno (Italy) *Tailoring catalytic activity of MoS_2 catalyst through functionalization with Brønsted-acid ligands: A Computational and experimental study for enhanced Hydrogen Evolution Reaction in Alkaline Media* Ida Ritacco,1, Giuseppe Santoriello1, Giulia Tuci2, Giuliano Giambastiani2, Matteo farnesi Camellone3, Lucia Caporaso1 1 Dipartimento di Chimica e Biologia, Università degli Studi di Salerno, via Giovanni Paolo II 132, 84084 Fisciano, Salerno, Italy 2 Institute of Chemistry of OrganoMetallic Compounds, ICCOM-CNR and Consorzio INSTM, Via Madonna del Piano, 10 - 50019, Sesto F.no, Florence, Italy. 3 Consiglio Nazionale delle Ricerche-Istituto Officina dei Materiali (CNR-IOM), 34136 Trieste, Italy
16:00 - 16:20	OR26	Wei Shi – Department of Materials Chemistry, Nagoya University, Furo-cho, Chikusa-ku, Nagoya (Japan) *Platinum-Tin Encapsulated Zeolite Catalysts with High Sn Loading: Boosted Performance in Methylcyclohexane Dehydrogenation* Wei Shi1, Akira Oda,1, Yuta Yamamoto2, Kyoichi Sawabe1, Atsushi Satsuma1 1Department of Materials Chemistry, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan. 2 Institute of Materials and Systems for Sustainability, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan.
16:20 – 16:40	OR27	Amir Yazdani – University of Genoa, DICCA, Genoa (Italy) *Development of a new perovskite electrocatalyst for solid oxide cells with a novel symmetrical geometry* Amir Yazdani1, Gabriella Garbarino1, Paola Riani2, Juan Basbus1, Maria Paola Carpanese1 1 University of Genoa, Department of Civil, Chemical and Environmental Engineering (DICCA), Via Opera Pia 15, 16145 Genoa, Italy. 2 University of Genoa, Department of Civil, Chemical and Environmental Engineering (DCCI), Via Dodecaneso 31, 16146 Genoa, Italy.
16:40 – 17:00	Coffee-Break	

		Short Orals
17:00 – 17:10	SO25	withdrawn
17:10 – 17:20	SO26	Andrea Fasolini – 1Dept. of Industrial Chemistry "Toso Montanari", University of Bologna, Bologna (Italy) *Cellulose Aqueous Phase Reforming (APR) using Ni and PtNi based catalyst for hydrogen generation: the unexpected effect of reductive atmosphere* Andrea Fasolini1, Jacopo De Maron1, Andreas Buono1, Eleonora Tosi Brandi1, Francesco Basile1, 1Dept. of Industrial Chemistry "Toso Montanari", University of Bologna, Bologna, Italy
17:20 – 17:30	SO27	Alberta Genco – Department of Engineering (DI), Viale delle Scienze, University of Palermo, Palermo (Italy) *TiO2 or Nb2O5 composites with graphene or graphene oxide as photocatalysts for Photoreforming of organics to obtain H2* Alberta Genco1,2, Elisa I. García-López3, Narimene Aoun1, Bartolo Megna1, Conchi O. Ania4, Giuseppe Marcì1 1 Department of Engineering (DI), Viale delle Scienze, University of Palermo, Palermo, Italy 2 Department of Chemistry, University of Perugia, Perugia, Italy 3 Department of Chemistry (STEBICEF) University of Palermo, Italy 4 POR2E Group, CEMHTI CNRS (UPR 3079), Université d'Orléans, 45071 Orléans, France
17:30 – 17:40	SO28	Sholpan Itkulova – D.V. Sokolsky Institute of Fuel, Catalysis, and Electrochemistry, Almaty (Kazakhstan) *Revealing the effect of Pd on Co-based catalysts in dry and bi-reforming of methane* Kuralay t. Tilegen1, 2, Sholpan S. Itkulova1,2, Yerzhan A. Boleubayev1, Aidana K. Aitzhanova1, Makpal A. Zhumash1 1D.V. Sokolsky Institute of Fuel, Catalysis, and Electrochemistry, 142, Kunaev str., Almaty, 050010, Kazakhstan
17:40 – 17:50	SO29	Valeria La Parola – Institute for NanoStructured Materials, Italian National Research Council (ISMN-CNR), Palermo (Italy) *Hydrogen production by chemical looping methane pyrolysis* Luca Consentino1,2, Francesca Deganello2, Rut Guil-Lopez3, Valeria La Parola2, Leonarda Francesca Liotta2, Giuseppe Pantaleo2 1 Department of Biological, Chemical and Pharmaceutical Sciences and Technologies (STEBICEF), University of Palermo, V.le delle Scienze Ed. 17, 90128 Palermo, Italy; 2 Institute for NanoStructured Materials, Italian National Research Council (ISMN-CNR), Via Ugo La Malfa 153, 90146 Palermo, Italy, 3 Instituto de Catálisis y Petroleoquímica, Spanish National Research Council (ICP-CSIC), 28049 Madrid, Spain
17:50 – 18:00	SO30	Alessia Marino – University of L'Aquila, Department of Physical and Chemical Sciences, L'Aquila (Italy) *Biomass-derived Activated Carbon for H_2 storage: influence of solvent and doping agent on the adsorption properties* Alessia Marino1, Carlo Poselle Bonaventura2, Sara Sciarretta1, Giuseppe Conte2, Alfredo Aloise1, Chiara Pelosi3, Andrea Lazzarini1, Celia Duce3, Luca Bernazzani3, Alfonso Policicchio2, Marcello Crucianelli1 1 University of L'Aquila, Department of Physical and Chemical Sciences, via Vetoio, 67100, L'Aquila, Italy. 2 University of Calabria, Physics Department, Via Bucci, 87036, Rende, Cosenza, Italy. 3 University of Pisa, Department of Chemistry and Industrial Chemistry, Via Moruzzi, 56124, Pisa, Italy.

18:00 – 19:00 parallel to P1 session	ERC and projects session	**Room Isola - RI** 18:00-18:15 Nadine Vermorel, EU-ERC (Brussels, Belgium) *Funding opportunities for the ERC programme* 18:15:18:30 Štěpán Kment, Czech Adv. Techn. and Res.. Inst.(Olomouc, Czech Republic) *Presentation of the SUN4Fuel project* 18:30:18:45 Chiara Genovese, University of Messina (Italy) *Presentation of the ERC Synergy project SCOPE* 18:45:19:00 Rosalba Passalacqua, ERIC aisbl and UniME (Belgium, Italy) *Presentation of the EIC project GreenSwap*

03/06/2025		
Room PR - Plenary		
08:50 – 09:50	PL1	Hiromi Yamashita - The University of Osaka (Japan) *Design of nanostructured Catalysts for Sustainable Energy and Environmental Uses* Graduate School of Engineering, The University of Osaka, Suita, Osaka 565-0871, Japan
10:00 – 10:20	OR28	Oleksandr Astakhov – Photovoltaics (IMD-3), Forschungszentrum Jülich GmbH, Jülich, Germany *Assessment of solar-to-chemical efficiency using only electrolyzer characteristics Shortcut bridging electrochemistry and photovoltaics* Oleksandr Astakhov,1, Thérèse Cibaka1, Lars Wieprecht1, Uwe Rau1,2, Tsvetelina Merdzhanova1 1 Photovoltaics (IMD-3), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany. 2 Faculty of Electrical Engineering and Information Technology, RWTH Aachen University, Mies-van-der-Rohe-Straße 15, 52074 Aachen, Germany.
10:20 – 10:40	OR29	Giuseppina Cerrato – Dipartimento di Chimica, Università degli Studi di Torino, Torino (Italy) *Crystalline face engineering in diverse Bismuth Oxyhalides for enhanced amoxicillin removal from water* Giuseppina Cerrato1,2, Alessia Giordana1,2, Vincenzo Fabbrizio2,3, Melissa Greta Galloni2,3, Ermelinda Falletta2,3, Claudia Letizia Bianchi 2,3 1Dipartimento di Chimica, Università degli Studi di Torino, Via Pietro Giuria 7, 10125 Torino, Italy 2Dipartimento di Chimica, Università degli Studi di Milano, via C. Golgi 19, 20133, Milano, Italy 3Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), via Giusti 9, 50121 Florence, Italy
10:40 – 11:00	OR30	Petar Djinovic – National Institute of Chemistry, Ljubljana (Slovenia) *Modification of the methane dry reforming reaction mechanism during visible light illumination of the Ni/CeO_{2-x} catalyst* Kristijan Lorber1, Janez Zavašnik2, Jordi Sancho-Parramon3, Matej Bubaš1,3, Nataša Novak Tušar1,4 And Petar Djinović1,4 1 National Institute of Chemistry, Hajdrihova 19, Ljubljana, Slovenia 2 Institute Jožef Stefan, Jamova 39, Ljubljana, Slovenia 3Ruđer Bošković institute, Bijenička 54, Zagreb, Croatia 4University of Nova Gorica, Vipavska 13, Nova Gorica, Slovenia
11:00 – 11:20	Coffee-Break	
11:20 – 11:40	OR31	Hyeonjeong Kim – Pohang University of Science and Technology, Division of Environmental Science and Engineering, Pohang (Republic of Korea) *Ti-Nb Oxide Nanotube Arrays with Cathodic Engineering for Photoelectrochemical Water Treatment and Molecular Hydrogen Production* Hyeonjeong Kim, Doyeon Kim, Eunju Hwang, Kangwoo Cho Pohang University of Science and Technology, Division of Environmental Science and Engineering, 77 Chungamro, Namgu, Pohang, Republic of Korea

11:40 – 12:00	OR32	Makoto Ogawa – Kyoto University, Grad. Sch. of Eng., Kyoto (Japan) *Flux Synthesis of Layered Perovskite Oxyiodide Photocatalyst for Visible-Light-Driven Water Splitting* Makoto Ogawa1, Hajime Suzuki1, Kanta Ogawa1, Hiroki Ubukata1, Osamu Tomita1, Akinobu Nakada1, Shunsuke Nozawa2, Akinori Saeki3, Hiroshi Kageyama1, Ryu Abe,1 1 Kyoto University, Grad. Sch. of Eng., Kyoto daigaku-katsura, Nishikyo-ku, Kyoto, Japan. 2 Photon Factory (PF), Institute of Materials Structure Science (IMSS), High Energy Accelerator Research Organization (KEK), Tsukuba, Ibaraki 305-0801, Japan. 3 Department of Applied Chemistry, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan.
12:00 – 12:20	OR33	Jiajia Zhang – Division of Chemistry and Biological Chemistry, School of Chemistry, Chemical Engineering and Biotechnology, Nanyang Technological University, Singapore (Singapore) *Squeezing Water Molecular Network with Kosmotropic Chemistry to Enhance Nitrogen-to-Ammonia Electrofixation* Jiajia Zhang1, Zhi Zhong Ang1, Hiang Kwee Lee,1,2,3 1 Division of Chemistry and Biological Chemistry, School of Chemistry, Chemical Engineering and Biotechnology, Nanyang Technological University, 21 Nanyang Link, Singapore 637371, Singapore. 2 Institute of Materials Research and Engineering, The Agency for Science, Technology and Research (A∗STAR), 2 Fusionopolis Way, #08-03, Innovis, 138634, Singapore. 3 Centre for Hydrogen Innovations, National University of Singapore, E8, 1 Engineering drive 3, 117580, Singapore
		Short Orals
12:20 – 12:30	SO31	Alfredo Aloise – Department of Physical and Chemical Sciences, University of L'Aquila, L'Aquila (Italy) *Synthesis of Nano-Sil1/TiO_2NTs Composite photocatalyst* Rosalba Passalacqua1, Alfredo Aloise2, Alessia Marino2, Nicola Di Nicola2, Siglinda Perathoner1, Gabriele Centi1 1 University of Messina, Department of Chemical, Biological, Pharmaceutical and Environmental Sciences (ChiBioFarAm) & INSTM CASPE (Lab. of Catalysis for Sustainable Production & Energy), Viale F. Stagno d'Alcontres 31, 98166 Messina, Italy 2 Department of Physical and Chemical Sciences, University of L'Aquila, via Vetoio, Coppito 2 67100 L'Aquila, Italy
12:30 – 12:40	SO32	Giusy Dativo – University of Catania, Dep. of Chemical Sciences, Catania (Italy) *Modified Montmorillonite-based catalysts for the photothermo-catalytic reduction of CO_2 into solar fuels* Giusy Dativo,1, Salvatore Scirè1, Giuseppe Compagnini1, Roberto Fiorenza1 1University of Catania, Dep. of Chemical Sciences, Viale Andrea Doria 6, Catania, Italy.
12:40 – 12:50	SO33	Giuseppe Santoriello – Dept. Chemistry and Biology, University of Salerno, Fisciano (SA), Italy. *Theoretical insights on innovative solutions for CO_2RR with Fe-based single atom catalysts* Giuseppe Santoriello1, Ida Ritacco1, Giulia Tuci2, Giuliano Giambastiani3, Claudio Ampelli4, Siglinda Perathoner4, Gabriele Centi4, Matteo Farnesi Camellone5, Lucia Caporaso1. 1 Dept. Chemistry and Biology, University of Salerno, via G. Paolo II 132, 84084, Fisciano (SA), Italy. 2 Institute of Chemistry of OrganoMetallic Compounds, ICCOM-CNR, Via Madonna del Piano, 10 - 50019, Sesto F.no, Florence, Italy. 3 Dept. of Chemistry "Ugo Schiff", Università di Firenze, via della Lastruccia 3-13, Sesto Fiorentino, Italy 4 Dept. ChiBioFarm, University of Messina, 98166 Messina, Italy 5 Consiglio Nazionale delle Ricerche-Istituto Officina dei Materiali (CNR-IOM), 34136 Trieste, Italy

12:50 – 13:00	SO34	Serena Esposito – Department of Applied Science and Technology and INSTM Unit of Torino – Politecnico, POLITO, Torino (Italy) *Enhancing visible-light photocatalytic hydrogen evolution with sub-5 nm Fe-doped CeO_2 nanocrystals in confined spaces* Giuseppina Iervolino1, Olimpia Tammaro2, Marco Fontana2, Bruno Masenelli3, Anne D. Lamirand3, Vincenzo Vaiano1, Serena Esposito2 1 Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II 132, 84084 Fisciano, SA, Italy. 2 Department of Applied Science and Technology and INSTM Unit of Torino – Politecnico, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy. 3 INSA Lyon, Ecole Centrale de Lyon, CNRS, Universite Claude Bernard Lyon
13:00 – 15:00	Lunch Break	
15:00 – 15:20	OR34	Federica Menegazzo – Ca' Foscari University of Venice, Department of Molecular Sciences and Nanosystems, Venice (Italy) *Photocatalysts and essential oils: could they ever be friends?* Andrea Campostrini1,2, Teresa Botrè1,2, Sabrina Manente1, Pilar Bosch-Roig3, Elena Ghedini4, Michela Signoretto1,2, Federica Menegazzo,1,2 1 Ca' Foscari University of Venice, Department of Molecular Sciences and Nanosystems, Via Torino 155, 30172 Venice, Italy. 2 INSTM RUVe, Via Torino 155, 30172 Venice, Italy. 3 Universitat Politècnica de València, Instituto Universitario de Restauración del Patrimonio, Camí de Vera s/n, 46022 Valencia, Spain. 4 University of Bari, Chemistry Department, Via Orabona 4, 70126 Bari, Italy.
15:20 – 15:40	OR35	Eleonora Tosi Brandi – University of Bologna, Industrial Chemistry Department, Bologna (Italy) *Novel application of CuMg-based Layered Double Hydroxides as photocathodes for photoelectrocatalytic CO_2 conversion* Eleonora Tosi Brandi1, Andrea Fasolini1, Jacopo De Maron1, Nicola Sangiorgi2, Alex Sangiorgi2, Alessandra Sanson2, Francesco Basile1 1 University of Bologna, Industrial Chemistry Department, Viale del Risorgimento 4, 40136, Bologna, Italy. 2 National Research Council of Italy, Institute of Science, Technology and Sustainability for Ceramics (CNR-ISSMC), Via Granarolo 64, 48018, Faenza, Italy.
15:40 – 16:00	OR36	Tsvetelina Merdzhanova – IMD3-Photovoltaics, Forschungszentrum Jülich GmbH, Jülich (Germany) *Solar-driven CO_2 electroreduction with direct-coupled PV-EC in realistic operating cycles* Tsvetelina Merdzhanova1, Thérèse Cibaka1, Oleksandr Astakhov1 IMD3-Photovoltaics, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany
16:00 – 16:40	KN10	Tapio Salmi – Åbo Akademi, Laboratory of Industrial Chemistry and Reaction Engineering (TKR), Turku/Åbo (Finland) *Catalytic ozonation of pharmaceuticals – From experiments to modelling* Soudabeh Saied1,2, Pasi Tolvanen1, Vincenzo Russo1,3, Pasi Tolvanen1, Tapio Salmi1,3 1 Åbo Akademi, Laboratory of Industrial Chemistry and Reaction Engineering (TKR), FI-20500 Turku/Åbo, Finland 2 Linde + Robinson Laboratories, California Institute of Technology, Pasadena 91125, United States 3 Università di Napoli 'Federico II', Chemical Sciences, IT-80125 Napoli, Italy
16:40 – 17:00	Coffee-Break	
17:00 – 17:10	SO35	Elisabetta Fanizza – University of Bari A. Moro, Department of Chemistry, Bari (Italy) *Photocatalytically-regenerable hyper-crosslinked microporous adsorbent* Pierluigi Lasala,1 Khalid Tahla,1 Antonio Maglione,2 Antonia Cerbone,2,3 Serena Catullo, 1 Gaia Raffaele, 1Ombretta Giancaspro,1 Antonella Milella,1 Ilaria De Pasquale,4 Rachele Castaldo,2 Gennaro Gentile,2 Maria Lucia Curri, 1,.4,5 Elisabetta Fanizza,1,.4,5 1University of Bari A. Moro, Department of Chemistry, Via Orabona 4, 70126 Bari, Italy

		2 CNR- Institute of Polymers, Composites and Biomaterials (IPCB), Via Campi Flegrei 34, 80078 Pozzuoli (NA), Italy 3 University of Naples, Department of Chemical Science, Strada Comunale Cinthia, 26, 80126, Naples, Italy 4 CNR-Institute for chemical and physical processes (IPCF), Via Orabona 4, 70126 Bari, Italy 5 National Interuniversity Consortium of Materials Science and Technology, INSTM, Bari Research Unit, 70126, Bari, Italy
17:10 – 17:20	SO36	Dimitrios Giannakoudakis – Aristotle University of Thessaloniki, Department of Chemistry, Thessaloniki (Greece) *Additive-free photochemical upcycling of bio-based (micro)plastics into value added chemicals* Athanasia Kotsaridou, Dimitrios A. Giannakoudakis, Konstantinos Triantafyllidis Aristotle University of Thessaloniki, Department of Chemistry, Thessaloniki, Greece
17:20 – 17:30	SO37	Marianna Guagliano – Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta"- CMIC, POLIMI, Milano (Italy) *An iron-based biochar-supported catalyst for diclofenac degradation* Marianna Gualiano1, Christian de los Ríos2, Karla Jiménez-Bautista2, Virginia Muelas-Ramos2, Ana Bahamonde3, Cinzia Cristiani1, Simone Pedrazzi4, Marco Puglia4, Daphne Hermosilla2, Antonio Gascó2 1 Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta"- CMIC, Politecnico di Milano, Piazza Leonardo Da Vinci 32, 20133, Milano, Italy 2 G-Aqua Research Group, Universidad Politécnica de Madrid, Escuela Técnica Superior de Ingeniería de Montes, Forestal y del Medio Natural, Calle José Antonio Novais 10, 28040 Madrid, Spain 3 Instituto de Catálisis y Petroleoquímica, Consejo Superior de Investigaciones Científicas, Calle de Marie Curie 2, 28049 Madrid, Spain 4 Department of Engineering "Enzo Ferrari", Università degli Studi di Modena e Reggio Emilia | UNIMO, Via Università 4, 41121 Modena
17:30 – 17:40	SO38	Chiara Ingrosso – 1CNR-IPCF Sez. Bari, c/o Dept. of Chemistry, Università degli Studi di Bari, Bari (Italy) *Photocatalytic nanocomposites based on pyrene functionalized reduced graphene oxide in situ decorated with TiO_2 nanorods* C. Ingrosso,1 A. Disha,2 M. Dell'Edera,1 I. De Pasquale,1 G. V. Bianco,3 A. Milella,2 A. Grandolfo1,4,5 E. Mesto,5 E. Schingaro,5 M. Striccoli,1 E. Fanizza,1,2 R. Comparelli,1 M. L. Curri1,2 1 CNR-IPCF Sez. Bari, c/o Dept. of Chemistry, Università degli Studi di Bari, via Orabona 4, 70126 Bari, Italy 2 Dept. of Chemistry, Università degli Studi di Bari, via Orabona 4, 70126 Bari, Italy 3 CNR-NANOTEC, c/o Università degli Studi di Bari, Via Orabona 4, 70126 Bari, Italy 4 Dept. of Electrical and Information Engineering, Polytechnic of Bari, Via Amendola 126/b, 70126 Bari, Italy 5 Dept. of Earth and Geoenvironmental Sciences, Università degli Studi di Bari, via Orabona 4, 70126 Bari, Italy
17:40 – 17:50	SO39	Luca Maistrello – Department. Of Chemistry, University of Studies of Milan, Milan(Italy) *Innovative Photoelectrocatalytic filter for Recirculating Aquaculture Systems* Luca Maistrello, 1 Simone Livolsi1 Eleonora Buoio,2 Daniela Bertotto3, Giuseppe Radaelli3, Alessia di Giancamillo,2 Annamaria Costa,2 Gian Luca Chiarello,1 1 Department. Of Chemistry, University of Studies of Milan, Via Golgi 19 20133, Milan (Italy) 2 Department of Veterinary Medicine and Animal Sciences, University of Milan, 26900 Lodi, Italy
17:50 – 18:00	SO40	Matteo Miceli – University of Messina (UNIME), CASPE/INSTM and ERIC aisbl, (ChiBioFarAm), Messina (Italy) *Sustainable ammonia synthesis using graphene/$MnFe_2O_4$-based gas-diffusion electrodes via photo-, electro-, and photo-electro-catalytic routes*

		Clécia Andrade Dos Santos1,2, Matteo Miceli,3, Luciane Pimenta Cruz Romão2, Maria Valnice Boldrin Zanoni2, Siglinda Perathoner3, Gabrieli Centi3, Claudio Ampelli3 1 São Paulo State University (UNESP), Institute of Chemistry, Araraquara, Brazil. 2 National Institute of Alternative Technologies for Detection, Toxicological Evaluation and Removal of Micropollutants and Radioactive Substances (INCT-DATREM), São Paulo State University (UNESP), Institute of Chemistry, Araraquara, Brazil. 3 University of Messina (UNIME), CASPE/INSTM and ERIC aisbl, Department of Chemical, Biological, Pharmaceutical and Environmental Sciences (ChiBioFarAm), Messina, Italy.
18:00 – 19:00	CH, P2	Poster session (Hallway) - P2

03/06/2025		
Room Massimo (RM)		
10:00 – 10:20	OR20 subst. OR37	Luke Harvey – The University of Newcastle, Chemical Engineering, University Drive, Callaghan, Australia *Enhanced Bio-Oil Upgrading: Mesoporous and Zeolitic Catalysts for Polyaromatic Hydrocarbon Conversion* Luke Harvey, Thoams Doyle, Rahim Kamari, Eric Kennedy, Michael Stockenhuber The University of Newcastle, Chemical Engineering, University Drive, Callaghan, Australia
10:20 – 10:40	OR38	Lingxi Zhou – State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing (China) *Intrinsic metal-support interactions break the activity-stability dilemma in electrocatalysis* Lingxi Zhou1, Menghao Yang2, Yihong Liu2, Feiyu Kang3,4 and Ruitao Lv1,4 1 State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing, China 2 Shanghai Key Laboratory for R&D and Application of Metallic Functional Materials, School of Materials Science and Engineering, Tongji University, Shanghai, China 3 Institute of Materials Research and Shenzhen Geim Graphene Center, Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen, China 4 Key Laboratory of Advanced Materials (MOE), School of Materials Science and Engineering, Tsinghua University, Beijing, China
10:40 – 11:00	OR39	Maria Elena Azzoni – Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, POLIMI, Milano (Italy) *N_2O decomposition on Fe/CHA catalyst using transient response methods* Maria Elena Azzoni1, Nicola Usberti1, Andrea Gjetja1, Isabella Nova1, Enrico Tronconi1, Roberta Villamaina2, Maria Pia Ruggeri2, Veselina Georgieva2, Loredana Mantarosie2, Jill Collier2 1 Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, Via La Masa, 34, 20156 Milan, Italy 2 Johnson Matthey Technology Centre, Blounts Court Road, Sonning Common, Reading RG4 9NH, UK
11:00 – 11:20	Coffee-Break	
11:20 – 11:40	OR40	Li-Yi Chen – New Materials Research & Development Department, China Steel Corporation, Kaohsiung City (Taiwan) *Pilot-Scale Evaluation of a Multi-Promoters Modified V/Ti-Based SCR Catalyst for Medium-Low Temperature DeNOx in Coking Plant Flue Gas* Li-Yi Chen, Chi-Lang Chen, Wen-Chang Chen New Materials Research & Development Department, China Steel Corporation, No. 1, Zhonggang Rd., Xiaogang Dist., Kaohsiung City, Taiwan
11:40 – 12:00	OR41	Alice Gramegna – Chemical Plants and Industrial Chemistry Group, Dip. Chimica, Università degli Studi di Milano, Milan (Italy) *New Technologies for Sustainable Valorisation of CH_4 and CO_2 from Livestock and Biogas*

		Ilenia Rossetti1,2, Alice Gramegna1,2, Matteo Tommasi1, Simge Naz Degerli2, Gianguido Ramis 3 1 Chemical Plants and Industrial Chemistry Group, Dip. Chimica, Università degli Studi di Milano, Via C. Golgi 19, 20133 Milan, Italy 2 INSTM Unit Milano-Università, Via C. Golgi 19, 20133 Milan, Italy 3 DICCA, Università degli Studi Genova, via all'Opera Pia 15A, 16145 Genoa, Italy
12:00 – 12:20	OR42	Tetyana Zheleznyak – University of Chemistry and Technology, Dept. of Chemical Engineering, Technická 5, Prague (Czech Republic) *Modeling of Cu/SSZ-13 SCR catalyst sulfation depending on HTA-induced changes in ZCuOH and Z2Cu site distribution* Tetyana Zheleznyak1, Petr Kočí,1, William S. Epling2 1University of Chemistry and Technology, Dept. of Chemical Engineering, Technická 5, Prague, Czech Republic. 2 University of Virginia, Dept. of Chemical Engineering, 385 McCormick Rd, Charlottesville, USA.
		Short Orals
12:20 – 12:30	SO41	Marco Francesco Torre – ChiBioFarAm – University of Messina, ERIC aisbl and CASPE/INSTM, Messina (Italy) *Plasma-assisted electrochemical conversion of nitrogen to ammonia under ambient conditions* Marco Francesco Torre,1, Lavanya Veerapuram1, Francesco Tavella1, Siglinda Perathoner1, Gabriele Centi1, Chiara Genovese1, Claudio Ampelli1 1 Department of Chemical, Biological, Pharmaceutical and Environmental Sciences (ChiBioFarAm) – University of Messina, ERIC aisbl and CASPE/INSTM, V.le F.Stagno d'Alcontres, 31 – 98166 Messina, Italy
12:30 – 12:40	SO42	Xuerui Zheng – Department of Interdisciplinary Engineering Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka (Japan) *Application of Manganese oxides support on Zeolite Y Catalysts in Benzene Total Oxidation* Xuerui ZHENG1, Hisahiro EINAGA,2 1 Department of Interdisciplinary Engineering Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka, Japan. 2 Department of Material Sciences, Faculty of Engineering Sciences, Kyushu University, Kasuga, Fukuoka, Japan.
12:40 – 12:50	SO43	Magdalena Żurowska – Faculty of Chemistry, Jagiellonian University, Kraków (Poland) *Uniform $SiO2@CeO_2$ core-shell structures doped with CuO and Co3O4 as efficient catalysts for toluene combustion* Magdalena Żurowska,1,2 , Anna Rokicińska1, Dominika Aśniowska1, Marek Dębosz1, Piotr Kuśtrowski1 1 Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, Kraków, Poland. 2 Doctoral School of Exact and Natural Sciences, Jagiellonian University, Łojasiewicza 11, Kraków, Poland.
12:50 – 13:00	SO44	Stephane Siffert – Unité de Chimie Environnementale et Interactions sur le Vivant (UCEIV UR 4492), Université du Littoral Côte d'Opale, Dunkerque (France) *Enhancing Catalytic Activity through Manganese Addition in Co or Cu Mixed Oxides for catalytic treatment of wood combustion emissions* C.E. Bounoukta1, C. Paris1, M. Tannous1, É. Genty1, F. Devred2, C. Poupin1, S. Siffert1, É. Gaigneaux2, R. Cousin1 1 Unité de Chimie Environnementale et Interactions sur le Vivant (UCEIV UR 4492), Université du Littoral Côte d'Opale, 145 avenue Maurice Schumann 59140 Dunkerque (France) 2 Institute of Condensed Matter and Nanosciences, Place Pasteur 1, L4.01.09, B-1348 Louvain-la-Neuve (Belgium)
13:00 – 15:00	Lunch Break	
15:00 – 15:40	KN5	Marco Daturi – Université de Caen Normandie, ENSICAEN, CNRS, LCS, Laboratoire Catalyse et Spectrochimie, Caen (France)

		Room temperature reduction of NO without reductants on iron Metal-Organic Frameworks Marco Daturi,1, Vanessa Blasin-Aubé1, Ji Wong Yoon1,2, Philippe Bazin1, Alexandre Vimont1, Jong-San Chang1,2, Stefan Wuttke1,4,5, Christian Serre5 1 Université de Caen Normandie, ENSICAEN, CNRS, LCS, Laboratoire Catalyse et Spectrochimie, 14000 Caen, France. 2 Catalysis Center for Molecular Engineering, Korea Research Institute of Chemical Technology (KRICT); Jang-dong 100, Yuseong, Daejeon, 305-600, South Korea. 3 Department of Chemistry, Sungkyunkwan University; Suwon, 440-476, South Korea 4 Ikerbasque, Basque Foundation for Science, Bilbao 48009, Spain & BCMaterials, UPV/EHU, Science Park, Leioa 48940, Spain 5 Institute of Porous Materials from Paris, ENS, ESPCI Paris, CNRS, PSL University, Paris 75005, France
15:40 – 16:00	OR43	Angiolina Comotti – University of Milano-Bicocca, Dept. of Materials Science, Milan (Italy) *Porous Materials and CO_2 capture* Silvia Bracco1, Jacopo Perego1, Charl X. Bezuidenhout1, Armando Rigamonti1,2, Angiolina Comotti,1 1University of Milano-Bicocca, Dept. of Materials Science, Via R. Cozzi 55, Milan, Italy. 2 University of Messina, Dept. of Chem., Biol., Pharm. and Environ. Sciences, Via F. Stagno d'Alcontres 31, Messina, Italy.
16:00 – 16:20	OR44	Takuma Higo – Waseda University, Department of Applied Chemistry, Shinjuku, Tokyo (Japan) *N_2O decomposition using an electric-field-assisted catalysis at low temperatures* Takuma Higo1, Ayaka Shigemito1, Yuki Inoda1, Chihiro Ukai, Kenta Mitarai2, Yasushi Sekine,1 1Waseda University, Department of Applied Chemistry, Shinjuku, Tokyo, Japan.
16:20 – 16:40	OR45	Marc Maurer – Karlsruhe Institute of Technology (KIT), Institute of Catalysis Research and Technology (IKFT), Karlsruhe (Germany) *Effect of promoters on the performance of Pt/TiO_2 catalyst for NOx removal by selective catalytic reduction (SCR) with H_2* Marc Maurer1, Maria Casapu2, Jan-Dierk Grunwaldt1,2 1Karlsruhe Institute of Technology (KIT), Institute of Catalysis Research and Technology (IKFT), Hermann-von-Helmholtz-Platz 1, Karlsruhe, Germany. 2 Karlsruhe Institute of Technology (KIT), Institute for Chemical Technology and Polymer Chemistry (ITCP), Engesserstraße 20, Karlsruhe, Germany.
16:40 – 17:00	Coffee-Break	
		Short Orals
17:00 – 17:10	SO45	Thaieny Zucolotto – University of São Paulo, Department of Chemical Engineering, São Paulo (Brazil) *Comparative Study of SBA-15 and CNT Supports for Iron Catalysts in Fischer-Tropsch Synthesis* Thaieny Zucolotto,1, Martin Schmal1, Anna Zimina2, Jan-Dierk Grunwaldt2, Reinaldo Giudici1 1University of São Paulo, Department of Chemical Engineering, Av. Prof. Luciano Gualberto, travessa 3, n. 380, São Paulo, Brazil. 2 Karlsruhe Institute of Technology, Department of Catalysis and Operando Spectroscopy, Hermann-von-Helmholtz-Platz - 76344, Karlsruhe, Germany.
17:10 – 17:20	SO46	withdrawn
17:20 – 17:30	SO47	Alessia Cometto – Politecnico di Torino, Department of Applied Science and Technology (DISAT), Turin (Italy) *Investigating Acidic Supports for Site-Selective Platinum Nanoparticles in VOC Oxidation* Alessia COMETTO1, Enrico Sartoretti1, Nunzio Russo1, Samir Bensaid1.

		1Politecnico di Torino, Department of Applied Science and Technology (DISAT), Corso Duca degli Abruzzi 24, 10129 Turin, Italy.
17:30 – 17:40	SO48	Renaud Cousin – Unité de Chimie Environnementale et Interactions sur le Vivant (UCEiV), Université du Littoral Côte d'Opale (ULCO), Dunkerque (France) *Impact of Cu/Mn ratio for CuMnOx prepared by oxalate coprecipitation: the essential point for total oxidation of model pollutants issued from biomass combustion* Julien Machinski1, Eric Genty1, Charf Eddine Bounoukta1, Christophe Poupin1, Valeria La Parola2, Stéphane Siffert1, Elise Berrier3, Leonarda Francesca Liotta2, Renaud Cousin1 1 Unité de Chimie Environnementale et Interactions sur le Vivant (UCEiV), Université du Littoral Côte d'Opale (ULCO), Dunkerque, 59140, France 2 Institute for the Study of Nanostructured Materials (ISMN)-CNR, Via Ugo La Malfa, 153, Palermo, 90146, Italy 3 Unité de Catalyse et Chimie du Solide (UCCS), UMR 8181, Université de Lille, CNRS, Centrale Lille, Université Artois, Lille, 59000, France
17:40 – 17:50	SO49	Federica De Luca – 1ERIC aisbl and CASPE/INSTM, Dpt. ChiBioFarAM University of Messina, Messina (Italy) *Citrus Waste to Carbon Catalysts: A Sustainable Approach to CO_2 Reduction* Federica De Luca,1 Palmarita Demoro,1 Imen Sghaier,1 Izuchica Nduka,2 Rosa Arrigo,2 Siglinda Perathoner,1 Gabriele Centi1, Salvatore Abate 1 1 ERIC aisbl and CASPE/INSTM, Dpt. ChiBioFarAM University of Messina Viale F. Stagno D'Alcontres 31, Messina, 98166, Italy 2 School of Science, Engineering and Environment University of Salford M5 4WT, Manchester, UK
17:50 – 18:00	SO50	Alessandro Allegri – Alma Mater Studiorum – University of Bologna, Department of Industrial Chemistry "Toso Montanari", C3 – Center for Chemical Catalysis, CIRI-FRAME, Bologna (Italy) *Rational optimisation of biomass-derived γ-valerolactone cascade synthesis* Alessandro Allegri1, Luca Ciacci1, Fabrizio Passarini1, Andrea Brigliadori2, Claudio Oldani3, Giuseppe Fornasari1, Stefania Albonetti1 1 Alma Mater Studiorum – University of Bologna, Department of Industrial Chemistry "Toso Montanari", C3 – Center for Chemical Catalysis, CIRI-FRAME, Via P. Gobetti 85, Bologna, Italy. 2 CNR-ISSMC (Former ISTEC), National Research Council of Italy-Institute of Science, Technology and Sustainability for Ceramics, Faenza, Italy. 3 Syensqo, Bollate, Italy.
18:00 – 19:00	CH P2	Poster session (Hallway) P2

03/06/2025		
Room Isole (RI)		
10:00 – 10:20	OR46	Raffaele Cheula – 1Aarhus University, Center for Interstellar Catalysis, Aarhus (Denmark) *Design of catalysts for CO_2 hydrogenation with fine-tuned machine learning potentials* Raffaele Cheula1, Jonh Kitchin2, And Mie Andersen1 1 Aarhus University, Center for Interstellar Catalysis, 8000 Aarhus, Denmark. 2 Carnegie Mellon University, Department of Chemical Engineering, 15213 Pittsburgh (PA), USA.
10:20 – 10:40	OR47	Giovanni Di Liberto – Università degli Studi di Milano Bicocca, Department of Materials Science, Milano (Italy) *Modeling Single-Atom Catalysis* Giovanni Di Liberto, Clara Saetta, Elisabetta Inico, Silvia Picello, Gianfranco Pacchioni Università degli Studi di Milano Bicocca, Department of Materials Science, Via Cozzi 55, Milano, Italy.

10:40 – 11:00	OR48	Shin Kihyun – Department of Materials Science and Engineering, Hanbat National University, Daejeon (Republic of Korea) *Beyond Linear Scaling: Innovations in Catalyst Optimization* Kihyun Shin1, Hyun You Kim2, Kyubock Lee3 1 Department of Materials Science and Engineering, Hanbat National University, Daejeon 34158, Republic of Korea 2 Department of Materials Science and Engineering, Chungnam National University, Daejeon 34134, Republic of Korea 3 Graduate School of Energy Science and Technology, Chungnam National University, Daejeon 34134, Republic of Korea
11:00 – 11:20	Coffee-Break	
11:20 – 12:00	KN6	Yuefeng Liu – Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian (China) *Generation of oxide surface patches promoting H-spillover in Ru/(TiOx)MnO catalysts enables CO_2 reduction to CO* Hui Kang,1 Shiyan Li,1 Jun Ma,1 Xuxu Zhai,1 Siglinda Perathoner,2 Gabriele Centi,2 Yuefeng Liu ,1 1 Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China 2 Department of ChiBioFarAm, University of Messina, Messina 98166, Italy
12:00 – 12:20	OR49	Elena Groppo – Department of Chemistry, INSTM and NIS Centre, University of Torino, Torino (Italy) *CO-induced dynamic behavior of supported PGM nanoparticles in mild conditions* Alberto Ricchebuono,1 Elena Seminerio,1 Paolo Lazzarini,1 Eleonora Vottero,1 Daniele Bonavia,1,2,3 Riccardo Pellegrini,4 Valentina Crocellà,1 Natale Gabriele Porcaro1 Stefano Checchia,3 Davide Ferri,4 Andrea Piovano,5 Elena Groppo1 1 Department of Chemistry, INSTM and NIS Centre, University of Torino, via Quarello 15A, Torino, I-10135, Italy 2 ESRF-The European Synchrotron, 71 avenue des Martyrs, Grenoble, 38000, France 3 Paul Scherrer Institut, Forschungsstrasse 111, 5232 Villigen PSI (Switzerland)5 4 Chimet SpA - Catalyst Division, Viciomaggio (Arezzo), I-52041, Italy 5 Institut Laue-Langevin (ILL), 71 avenue des Martyrs, Grenoble, 38000, France
		Short Orals
12:20 – 12:30	SO51	Alessandra Beretta – Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, POILIMI, Milano (Italy) *A multiscale study of CH4 pyrolysis over Fe-Al2O3 catalyst: the challenge of C build-up for the kinetic and the reactor studies* Marco Orsenigo1, Davide Cafaro1, Veronica Piazza1, Chiara Negri1, Lidia Castoldi1, Gianpiero Groppi1, Matteo Maestri1, Alessandra Beretta,1 1Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, Via La Masa, 34 – 20156 Milano, Italy.
12:30 – 12:40	SO52	Elisabetta Inico – Università degli Studi di Milano-Bicocca, Dipartimento di Scienza dei Materiali, Milano (Italy) *Combining ab-initio thermodynamics and kinetics toward the Oxygen Evolution and Reduction Mechanism on a Dual Atom Catalyst* Elisabetta Inico1, Giovanni Di Liberto1, Gianfranco Pacchioni1 1Università degli Studi di Milano-Bicocca, Dipartimento di Scienza dei Materiali, Via R. Cozzi 55, 20125 Milano, Italy
12:40 – 12:50	SO53	Luca Mastrianni – Università di Napoli 'Federico II', Chemical Sciences, Napoli (Italy) *DLP 3D printing of catalyst architectures: from material preparation to mathematical modeling of structure effects on catalyst performance* Luca Mastroianni1,2, Ananias Medina2, Anna De Domenico1,2, Kari Eränen2, Martino Di Serio1, Dmitry Murzin2, Vincenzo Russo1,2, Tapio Salmi1,2 1Università di Napoli 'Federico II', Chemical Sciences, IT-80125 Napoli, Italy 2Åbo Akademi, Laboratory of Industrial Chemistry and Reaction Engineering (TKR), FI-20500 Turku/Åbo, Finland

14:50 – 13:00	SO54	Mauro Bacconi – POLIMI, Laboratory of Catalysis and Catalytic Processes, Department of Energy, Milano (Italy) *Hierarchical multiscale analysis of CO_2 electroreduction at high current densities: The onset of transport limitations* Kaustav Niyogi, Mauro Bracconi, Matteo Maestri Politecnico di Milano, Laboratory of Catalysis and Catalytic Processes, Department of Energy, Via La Masa 34, Milano 20156, Italy
13:00 – 14:55	Lunch Break	
14:55 – 15:00	INTRO	Premio "Pio Forzatti" Alessandra Beretta - Introduction
15:00 – 15:20	OR50	Daria Gashnikova – Karlsruhe Institute of Technology, Institute for Chemical Technology and Polymer Chemistry, Karlsruhe (Germany) *Confining Pd on CeO_2 nano-islands for more efficient oxidation catalysts* Daria Gashnikova1, Florian Maurer1, Maria Casapu1, Jan-Dierk Grunwaldt1,2 1 Karlsruhe Institute of Technology, Institute for Chemical Technology and Polymer Chemistry, Karlsruhe, Germany. 2 Karlsruhe Institute of Technology, Institute of Catalysis Research and Technology, Karlsruhe, Germany.
15:20 – 15:40	OR51	Running Kang – State Key Laboratory of High-Temperature Gas Dynamics, Institute of Mechanics, Chinese Academy of Sciences, Beijing (China) *Investigation on structure-activity relationship and reaction pathways of CuO/CeO_2 catalysts for NH3 self-sustained combustion* Running Kang1, Mingxia Yang1,2, Zirui Zhang1, Chenhang Zhang1,3, Xiaokun Yi1, Feng Bin1, Xiaolin Wei1 1State Key Laboratory of High-Temperature Gas Dynamics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, PR China. 2 School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, PR China. 3 Key Laboratory of Beijing on Regional Air Pollution Control, Faculty of Environment and Life, Beijing University of Technology, Beijing 100124, PR China
15:40 – 16:00	OR52	Patrick Lott –KIT, Institute for Chemical Technology and Polymer Chemistry, Karlsruhe (Germany) *Forced dynamic reactor operation for boosting the activity and selectivity of Pd-based ammonia oxidation catalysts* Camilo Cárdenas1, Thomas Häber2, Olaf Deutschmann1,2, Patrick Lott1 1 Karlsruhe Institute of Technology (KIT), Institute for Chemical Technology and Polymer Chemistry, Engesserstr. 20, 76131, Karlsruhe, Germany. 2 Karlsruhe Institute of Technology (KIT), Institute of Catalysis Research and Technology (IKFT), Hermann-von-Helmholtz-Platz 1, 76344, Eggenstein-Leopoldshafen, Germany.
16:00 – 16:20	OR53	Dieter Plessers – KU Leuven, Center for Sustainable Catalysis and Engineering, Leuven (Belgium) *Spectroscopic Investigation of the Role of Water in Copper Zeolite Methane Oxidation* Dieter plessers,1, alexander j. Heyer2, jing ma1, augustin braun2, hannah m. Rhoda2, max l. Bols1, robert a. Schoonheydt1, edward i. Solomon2, bert f. Sels1 1KU Leuven, Center for Sustainable Catalysis and Engineering, Celestijnenlaan 200F, Leuven, Belgium. 2 Stanford University, Department of Chemistry, 337 Campus Drive, Stanford, U.S.A.
16:20 – 16:40	OR54	Yulong Shan – Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing (China) *Aluminum-rich small-pore Cu-zeolites applied for NH_3-SCR of NOx* Yulong Shan, Guangzhi He, Wenpo Shan, Yunbo Yu, Hong He 1Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Haidian District, Beijing, 100085, China.
16:40 – 17:00	Coffee-Break	
		Short Orals

17:00 – 17:10	SO55	Christoph Hahn – Institute of Energy Process Engineering and Chemical Engineering, Chair of Reaction Engineering, TU Freiberg, Freiberg (Germany) *Modelling the combined HCHO/SCR reaction on $V_2O_5/WO_3/TiO_2$ catalyst in lean gas engine exhaust* Christoph HAHN1, Sven KURETI1, Institute of Energy Process Engineering and Chemical Engineering, Chair of Reaction Engineering, TU Freiberg, Fuchsmuehlenweg 9D, 09599 Freiberg, Germany
17:10 – 17:20	SO56	Ilyas Yousuf Mir – Indian Institute of Technology Delhi, Department of Chemical Engineering, Hauz Khas, New Delhi (India) *Microkinetic modelling of a Pd-based three-way catalyst for stoichiometric natural gas vehicles* Ilyas Yousuf Mir1, Divesh Bhatia,1 1Indian Institute of Technology Delhi, Department of Chemical Engineering, Hauz Khas, New Delhi 110016, India
17:20 – 17:30	SO57	Yuki Inoda – Department of Applied Chemistry, Waseda University, Shinjuku, Tokyo (Japan) *NOx storage and reduction system with an electric field at low temperature* Yuki Inoda1, Ayaka Shigemoto1, Chihiro Ukai1, Takuma Higo1, Kohei Oka2, Yasushi Sekine,1 1 Department of Applied Chemistry, Waseda University, 3-4-1, Okubo, Shinjuku, Tokyo, 169-8555, Japan. 2 Isuzu Central Research Center, Fujisawa, Kanagawa, Japan.
17:30 – 17:40	SO58	Enrico Sartoretti – POLITO, Dept. of Applied Science and Technology, Turin (Italy) *Pd-ceria catalysts for complete CH_4 oxidation: influence of Pr-doping on sulfur resistance* Enrico Sartoretti, Eleonora Calì, Chiara Novara, Nunzio Russo, Debora Fino, Samir Bensaid Politecnico di Torino, Dept. of Applied Science and Technology, C.so Duca degli Abruzzi 24, Turin, Italy.
17:40 – 17:50	SO59	Jieling Shao – Chemistry and Chemical Engineering, Competence Centre of Catalysis, Chalmers University of Technology, Gothenburg (Sweden) *Pd speciation and support effect for H_2 SCR* Jieling Shao1, Zhipeng Wang,2 Phuoc Hoang Ho1, Yifei Ren2, Derek Creaser1, Feng Wang2 and Louise Olsson1 1Chemistry and Chemical Engineering, Competence Centre of Catalysis, Chalmers University of Technology, Gothenburg S041296, Sweden. 2 Department of Chemical Engineering, University College London, London WC1E 7JE, United Kingdom
17:50 – 18:00	SO60	Shivangi Singh – Department of Physics and Competence Centre for Catalysis, Chalmers University of Technology, Göteborg (Sweden) *Water Inhibition of NH_3-SCR over Cu-CHA: Measurements and DFT-based kinetic modeling* Shivangi Singh,a,b Yingxin Fenga, Ton V. W. Janssensb, and Henrik Grönbecka A Department of Physics and Competence Centre for Catalysis, Chalmers University of Technology, SE-412 96 Göteborg, Sweden B Umicore Denmark ApS, DK-2970 Hørsholm, Denmark
18:00 – 18:30	Special Guest Lecture	**Room Isola - RI** Michael Stockenhuber *The Nexus between Understanding Redox Catalysts and Process Development for Environmental Applications.* Michael Stockenhuber, Luke Harvey, Matthew Drewery, Eric Kennedy University of Newcastle and UTS University - Sidney, Australia
18:30 – 19:00	Exhibitors session	**Room Isola - RI** 18:30-18:45 Labtech: Innovation, Technology, your solution! (M. Musetti) 18.45-19:00 Verder Sci. (S. Tieuli)

04/06/2025		
Room PR - Plenary		
08:50 – 09:50	PL2	Olaf Deutschmann – KIT, Karlsruhe (Germany) *Dynamics in environmental catalysis: from surface coverages to reactor operation* Patrick Lott and Olaf Deutschmann Karlsruhe Institute of Technology (KIT), Karlsruhe (Germany)
10:00 – 10:20	OR55	Stefania Albonetti – University of Bologna, Department of Industrial Chemistry "Toso Montanari", C3 – Center for Chemical Catalysis, CIRI-FRAME, Bologna, (Italy) *Tuning the properties of Pt/Ni supported catalysts for the reductive amination of furfural* F. Liuzzi1, C. Cesari1, N. Dimitratos1,2, S. Zacchini1,2, S. Albonetti1,2 1 University of Bologna, Department of Industrial Chemistry "Toso Montanari", 2 C3 – Center for Chemical Catalysis, CIRI-FRAME, Via P. Gobetti 85, Bologna, Italy
10:20 -10:40	OR56	Irina Ivanova – Department of Chemistry, Lomonosov Moscow State University, Moscow (Russia) *Catalytic transformation of levulinic acid and C6-carbohydrates to γ-valerolactone over Zr- and Sn-containing BEA zeolites obtained by green ultra-fast synthesis* I.I. Ivanova, R.Yu. Barakov, E. Andriako, I.A. Ermakov, A. Dubtsova Department of Chemistry, Lomonosov Moscow State University, Leninskiye Gory 1, bld. 3, 119991 Moscow, Russia
10:40 – 11:00	OR57	Domenico Licursi – University of Pisa, Department of Chemistry & Industrial Chemistry, Pisa (Italy) *Use of ternary Cu/Zn/La mixed oxides for the hydrogenation/hydrogenolysis of hexyl hexanoate to 1-hexanol aimed at overcoming the issues of chromium-based systems* Domenico Licursi, Leonardo Carmassi, Nicola Di Fidio, Sara Fulignati, Claudia Antonetti, Anna Maria Raspolli Galletti University of Pisa, Department of Chemistry & Industrial Chemistry, Via Giuseppe Moruzzi, 13, Pisa, Italy.
11:00 – 11:20	Coffee-Break	
11:20 – 12:00	KN7	Stefan Vajda – Department of Nanocatalysis, J. Heyrovsky Institute of Physical Chemistry, Czech Academy of Sciences, Prague (Czech Republic) *Bridging the materials space in CO2 conversion using model subnanometer clusters and nanometer size particles synthesized by wet chemistry* Stefan Vajda Department of Nanocatalysis, J. Heyrovsky Institute of Physical Chemistry., Czech Academy of Sciences, Dolejškova 2155/3, 18223 Prague, Czech Republic
12:00 – 12:20	OR58	Francesco Mauriello – Dipartimento DICEAM, Università degli Studi Mediterranea di Reggio Calabria, Reggio di Calabria (Italy) *Transfer Hydrogenation of Furfural Under Continuous Flow Conditions by Shvo Catalyst* Maitê Campos1, Luís Adriano Santos Do Nascimento1, Emilia Paone2, Giulia Brufani2,3, Chiara Lenzi4, Andrea Piazzi4, Rita Mazzoni4, Luigi Vaccaro3, Francesco Mauriello,2 1Universidade Federal do Pará UFPA, Department of Biotechnology, Augusto Corrêa Street, Belém, Brazil. 2 Dipartimento DICEAM, Università degli Studi Mediterranea di Reggio Calabria, Via Zehender, Reggio di Calabria, Italy. 3 Dipartimento di Chimica Biologia e Biotecnologie, Università degli Studi di Perugia, Via Elce di Sotto 8, Perugia 4 Dipartimento di Chimica Industriale, Università degli Studi Alma Mater Studiorum di Bologna, Viale Risorgimento 4, Bologna, Italy.
12:20 – 12:40	OR59	Ricardo Soares – Faculty of Chemical Engineering, Federal University of Uberlândia, Uberlândia, Minas Gerais (Brazil) *Guaiacol hydrodeoxygenation over Ni-Fe supported on Nb2O5 and SiO2 catalysts* Karen Lucia P. Pantoja1, Naiara da Costa Telis1,2, Gisele Cristina R. Silva1, Klaus Raffelt2, Ricardo R. Soares1, 1 Faculty of Chemical Engineering, Federal University of Uberlândia, Uberlândia, Minas Gerais, Brazil

		2 Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1. Eggenstein-Leopoldshafen
12:40 – 13:00	OR60	Martino di Serio – Università di Napoli 'Federico II', Chemical Sciences, Napoli (Italy) *Vegetable oil-based 5-membered cyclic carbonates as bio-based building blocks for NIPU foams: catalysis, synthesis and kinetic aspects* Martino Di Serio,1, Federica Orabona1,2, Tapio Salmi1,2, Vincenzo Russo1,2 1Università di Napoli 'Federico II', Chemical Sciences, IT-80125 Napoli, Italy 2Åbo Akademi, Laboratory of Industrial Chemistry and Reaction Engineering (TKR), FI-20500 Turku/Åbo, Finland
13:00 – 15:00	Lunch Break	
		Short Orals
15:00 – 15:10	SO61	Jennifer Cueto – Thermochemical Processes Unit, IMDEA Energy, Móstoles (Spain) *Catalytic co-pyrolysis of lignocellulose and non-edible vegetable oil using n-ZSM-5: synergistic effects for aromatic hydrocarbons production* Maurizio pagano1, 2, Jennifer Cueto1, Inés Moreno1, 2, David P. Serrano, 1, 2 1 Thermochemical Processes Unit, IMDEA Energy, 28935 Móstoles, Spain. 2 Chemical and Environmental Engineering Group, Rey Juan Carlos University, 28933 Móstoles, Madrid
15:10 – 15:20	SO62	Camilla Galletti – POLITO, Department of Applied Science and Technology (DISAT), Torino (Italy) *Exploring the technical and environmental potentialities of rice husk-derived biochar for H_2S removal* Francesca Demichelis, Premchand Premchand, Camilla Galletti, Fabio Alessandro Deorsola, Raffaele Pirone, Debora Fino, Guido Saracco Politecnico di Torino, Department of Applied Science and Technology (DISAT), Corso Duca degli Abruzzi 24, 10129 Torino, Italy
15:20 – 15:30	SO63	Andrea Di Giuliano – University of L'Aquila, Department of Industrial and Information Engineering and Economics, L'Aquila (Italy) *Green syntheses of Ni-Mo-Al catalysts for deoxygenation of vegetable oil into green diesel: green metrics of syntheses and deoxygenation performances* Andrea Di Giuliano ,1, Paola Pietrangeli 1, Stefania Lucantonio 1, Giuseppe Di Vito Nolfi 2, Katia Gallucci 1, & Leucio Rossi 2 1 University of L'Aquila, Department of Industrial and Information Engineering and Economics, Piazzale E. Pontieri 1, L'Aquila, Italy. 2 University of L'Aquila, Department of Physical and Chemical Sciences., Via Vetoio, L'Aquila, Italy.
15:30 – 15:40	SO120 moved	Anna Rokicińska – Faculty of Chemistry, Jagiellonian University, Kraków (Poland) *Catalytic behaviour of CuO and Co_3O_4 phases deposited on hollow@SiO_2 and @TiO_2 structures in toluene combustion* Anna Rokicińska,1, Magdalena Żurowska1,2, Radosław Sadowski1, Marek Dębosz1, Piotr Łątka1, Piotr Kuśtrowski1 1 Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, Kraków, Poland 2 Doctoral School of Exact and Natural Sciences, Jagiellonian University, Łojasiewicza 11, Kraków, Poland
		Orals
15:40 – 16:00	OR61	Jacopo De Maron – University of Bologna, "Toso Montanari" Industrial Chemistry Dept., Bologna (Italy) *Promoting zirconia with carbon: enhanced hybrid ZrO_2/C ketonization catalyst for the valorization of e-acetic acid* Jacopo De Maron1, Gaetano Maria D'onofrio1, Eleonora Tosib Randi1, Andrea Fasolini1, Gloria Gottardi2, Francesco Basile1, Fabrizio Cavani1, Tommaso Tabanelli1 1University of Bologna, "Toso Montanari" Industrial Chemistry Dept., Viale Risorgimento 4, Bologna, Italy. 2 Bruno Kessler Foundation, Center for Sustainable Energy., Via Sommarive 18, Trento, Italy.

16:00 – 16:20	OR62	J.A.Z. Pieterse – TNO Sustainable technology for industrial processes, Petten (The Netherlands) *Bifunctional catalysts for sorption-enhanced reaction processes* J.A.Z. Pieterse, G.D. Elzinga, S. Booneveld, V. Dikic TNO Sustainable technology for industrial processes, 1755 LE Petten, Netherlands
16:20 – 16:40	OR63	Amy Radford – Wolfson Catalysis Centre, University of Oxford, Oxford, England *Mechanistic Link to Electrode Magnetism in Magneto-Electrocatalytic Oxygen Evolution* Amy Radford1, Dorottya Szalay1, Chen Wu2, Yiyang Li1, Edman Tsang1 1Wolfson Catalysis Centre, University of Oxford, Oxford, England 2 School of Materials Science and Engineering, Zhejiang University, Hangzhou, China
16:40 – 17:00	Coffee-Break	
17:00 - 17:20	OR64	Sara Fulignati – University of Pisa, Department of Chemistry and Industrial Chemistry, Pisa (Italy) *Development of an innovative biorefinery process by the one-pot fractionation of defatted cardoon* Sara Fulignati,1, Francesca Barsotti1, Nicola Di Fidio1, Domenico Licursi1, Stefano Frigo2, Claudia Antonetti1, Anna Maria Raspolli Galletti1 1 University of Pisa, Department of Chemistry and Industrial Chemistry, via G. Moruzzi 13, Pisa, Italy. 2 University of Pisa, Department of Energy, System, Territory and Construction Engineering (DESTEC), Largo L.Lazzarino 1, Pisa, Italy
17:20 – 17:40	OR65	Nolven Guilhaume – IRCELYON, UMR5256 CNRS and University Claude Bernard Lyon 1, Villeurbanne (France) *Temperature mapping of fixed-bed reactor in microwave-assisted catalytic dry-reforming of methane over SiC-based catalysts* Andrea Merlo, Léon Thomann, Nolven Guilhaume, Yves Schuurman IRCELYON, UMR5256 CNRS and University Claude Bernard Lyon 1, Villeurbanne, France
17:40 – 18:00	OR66	Aqsa Noreen – Competence Center for Catalysis, Chemical Engineering, Chalmers University of Technology, Gothenburg (Sweden) *Zn-based catalyst route for Pentaerythritol synthesis: Process related CO_2 reduction* Aqsa Noreen.1 Derek Creaser.1, Oleg Pajalic.2, Louise Olsson1 1 Competence Center for Catalysis, Chemical Engineering, Chalmers University of Technology, SE-422096 Gothenburg, Sweden 2 Perstorp AB, Industriparken, 284 80 Perstorp, Sweden
		Short Orals
18:00 – 18:10	SO65	Giovanni Cardolini Rizzo – POLITO, Department of Applied Science and technology (DISAT), Torino (Italy) *Assessment of low PGM catalyst for Ammonia cracking* Giovanni Cardolini Rizzo , Carlo Castelli, Alessandro Monteverde. Politecnico di Torino,Department of Applied Science and technology (DISAT), Torino, Italy.
18:10 – 18:20	SO66	Theodoros Lyras – Centre for Research and Technology Hellas, Thessaloniki (Greece) *Parametric investigation of an electrified steam methane reforming process using CFD modelling* Theodoros Lyras, Panagiotis Drosatos, Nikos Nikolopoulos Centre for Research and Technology Hellas, 6th km Charilaou-Thermi Rd., 57001, Thessaloniki, Greece.
18:20 – 18:30	SO67	Claudia Antonetti – University of Pisa, Department of Chemistry and Industrial Chemistry, Pisa (Italy) *Fully Renewable Diphenolic Acid Production in Batch and Continuous Reactors in the presence of new biomass-derived acid catalysts and LCA assessment of the entire process* Benedetta Bertini1, Domenico Licursi1, Francesco Taddeo2, Alessandra Sessa3, Nicola Scotti4, Raffaele Cucciniello3, Vincenzo Russo2, Anna Maria Raspolli Galletti1, Claudia Antonetti,1

		1 University of Pisa, Department of Chemistry and Industrial Chemistry, Via G. Moruzzi 13, 56124 Pisa, Italy. 2 University of Naples Federico II, Department of Chemical Sciences, Via Cintia, 80126 Naples, Italy. 3 University of Salerno, Department of Chemistry and Biology, Via G. Paolo II 132, 84084 Fisciano, Italy. 4CNR, SCITEC "Giulio Natta", Via C. Golgi 19, 20133 Milano, Italy.
18:30 – 18:40	SO68	Carla Calabrese – CNR, Institute for the Study of Nanostructured Materials (ISMN), Palermo (Italy) *Heterogeneous catalysts based on hybrid POSS nanocages for sustainable applications* Michelangelo Gruttadauria,1, Carmela Aprile,2, Francesco Giacalone,1, Carla Calabrese,3,§ 1University of Palermo, Department of Biological, Chemical and Pharmaceutical Sciences and Technologies, Viale Delle Scienze, Ed. 17 90128, Palermo Italy. 2 University of Namur, Department of Chemistry, Namur Institute of Structured Matter (NISM), 61 rue de Bruxelles, Namur 5000, Belgium. 3 National Research Council of Italy, Institute for the Study of Nanostructured Materials (ISMN), Via Ugo La Malfa 153, 90146, Palermo, Italy.
18:40 – 18:50	SO69	Enrico Catizzone – Chemical Engineering Catalysis and Sustainable Processes Laboratory, University of Calabria, Rende (Italy) *Gasification of residual biomass in a rotary kiln reactor integrated with radio frequency plasma torch* Enrico Catizzone1, Cesare Freda2, Antonio Villone2, Assunta Romanelli2, Giacinto Cornacchia2 1Chemical Engineering Catalysis and Sustainable Processes Laboratory, University of Calabria, Rende, Italy. 2Laboratory of Thermochemical processes for waste and biomass, Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA), Trisaia Research Center, Rotondella, Italy.
18:50 – 19:00	SO70	withdrawn

04/06/2025		
Room Massimo - RM		
10:00 – 10:20	OR67	Joanna Gryboś – *Redox Behavior of Manganese Oxide Catalysts in Thermochemical Redox Cycles: Mechanistic Insights from In Situ TEM and DFT Investigations* Joanna Gryboś1, Karol Górecki, Monika Fedyna, Michał Pacia, Zbigniew Sojka 1Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Kraków, Polska.
10:20 – 11:00	KN8	Roberta Villamaina – Johnson Matthey Technology Centre, UK *Challenges and performance of Cu-SCR catalysts under H2-ICE conditions* Roberta Villamaina1, Maria Pia Ruggeri2, Paul Millington1, Husn Islam1, Lisa Allen1, David Bergeal2, Jill Collier1 1 Johnson Matthey Technology Centre, Blounts Court Road, RG4 9NH, UK 2 Johnson Matthey, Orchard Road, Royston, SG8 5H2, UK
11:00 – 11:20	Coffee-Break	
11:20 – 11:40	OR68	Simone Perego – Istituto Italiano di Tecnologia, Atomistic Simulations, Genoa (Italy) *Unraveling the catalytic activity of FeCo alloys for ammonia decomposition via molecular dynamic simulations* Simone Perego, Luigi Bonati, Michele Parrinello Istituto Italiano di Tecnologia, Atomistic Simulations, 16165 Genoa, Italy.
11:40 – 12:00	OR69	Silmina Silmina – Tokyo University of Agriculture and Technology, Graduate School of Bio-Applications and Systems Engineering, Nakacho, Tokyo (Japan) *Bio Oil Steam Reforming over Mesoporous Hexagonal and Noncapsular Ni Nanoparticle Catalyst Prepared Using Post Loading and Co-Assembly Strategy* Silmina Silmina, Naoko Suyama, Kenji Kamiya and Eika W. Qian

		Tokyo University of Agriculture and Technology, Graduate School of Bio-Applications and Systems Engineering, Nakacho, 2-24-16, Koganei, Tokyo 184-8588, Japan
12:00 – 12:20	OR70	Zbigniew Sojka – Faculty of Chemistry Jagiellonian University, Krakow (Poland) *Decomposition of N_2O on Redox-Tuned Cobalt Spinel Catalysts – Molecular Orbital Resolution of Reaction Mechanism* Leszek Nowakowski, Camillo Hudy, Filip Zasada, Zbigniew Sojka Faculty of Chemistry Jagiellonian University, ul. Gronostajowa 2, 30-387 Krakow, Poland
12:20 – 12:40	OR71	Felix Ott, RWTH Aachen University, Aachen (Germany) *Monitoring the active site of CeO_2 supported Pd by H_2-D_2 exchange and EXAFS* Felix Ott1, Chalachew Mebrahtu1,2, Regina Palkovits1,2 1 Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany 2 Institute for Sustainable Hydrogen Economy, Forschungszentrum Jülich GmbH, Jülich, Germany
12:40 – 13:00	OR11 subs. OR72	Choji Fukuhara - Department of Applied Chemistry and Biochemical Engineering, Graduate School of Engineering, Shizuoka University, Shizuoka (Japan) *Innovative CO_2 recycling system with powerful performance for converting GHG: Multi-stage structured catalyst system for methanation, dry reforming and carbon-capture* Choji Fukuhara, Yuki Yamada, Yu Nakazawa, Hiroshi Akama, Ryo Watanabe Department of Applied Chemistry and Biochemical Engineering, Graduate School of Engineering, Shizuoka University, 3-5-1 Johoku, Chuo-ku, Hamamatsu, Shizuoka, Japan
13:00 – 15:00	Lunch Break	
		Short Orals
15:00 – 15:10	SO71	Riccardo Colombo – POLIMI, Department of Energy, LCCP group, Milan (Italy) *Surface Carbon Formation and its Impact on Methane Dry Reforming Kinetics on Rhodium-Based Catalysts by Operando Raman Spectroscopy* Riccardo Colombo1, Gianluca Moroni1, Chiara Negri1, Matteo Monai2, Bert M. Weckhuysen2, Matteo Maestri1 1 Politecnico di Milano, Department of Energy, LCCP group, via La Masa 34, 20156 Milan, Italy 2 Utrecht University, Inorganic Chemistry and Catalysis Group, Universiteitsweg 99, Utrecht, The Netherlands
15:10 – 15:20	SO72	Elisabetta Petri – Dept. of Chemistry “Giacomo Ciamician”, University of Bologna, Bologna (Italy) *Valorization of different organic waste sources for electrochemical applications: Process and life cycle assessment* E. Petri1, S. El Yamani2,3, F. Capodarca1, A. Primante2,3, A. Contin2.3, F. Soavi1,3 1Dept. of Chemistry “Giacomo Ciamician”, University of Bologna, Via Selmi 2, 40126, Bologna, Italy 2 Dept. of Physics and Astronomy "Augusto Righi", University of Bologna, Viale Berti Pichat 6/2, 40127, Bologna 3Centre for the Environment, Energy, and Sea - Interdepartmental Centre for Industrial Research in Renewable Resources, Environment, Sea and Energy (CIRI-FRAME), University of Bologna, Viale Ciro Menotti 48, 48122, Marina di Ravenna, Italy
15:20 – 15:30	SO73	Elisabeth Herzinger – KIT, Institute of Catalysis Research and Technology (IKFT), Eggenstein-Leopoldshafen (Germany) *Bimetallic Platinum-Rhenium Catalysts: Enhancing Hydrogen Storage Efficiency through Material Optimization and Synthesis Modification* Elisabeth Herzinger, Hannah Park, Jennifer Weimann, Moritz Wolf Karlsruhe Institute of Technology (KIT), Institute of Catalysis Research and Technology (IKFT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany. and Engler-Bunte-Institut (EBI), Engler-Bunte-Ring 1, 76131 Karlsruhe, Germany.
15:30 – 15:40	SO74	Plaifa Hongmanorom – Institute of Condensed Matter and Nanoscience, UCLouvain, Louvain-La-Neuve (Belgium) *Spark-ablated metal nanoparticle catalysts supported on TiO_2 for CO_2 methanation* Plaifa Hongmanorom, Damien P. Debecker

		Institute of Condensed Matter and Nanoscience, UCLouvain, Place Louis Pasteur 1, Louvain-La-Neuve, Belgium.
		Orals
15:40 – 16:00	OR73	Ryo Watanabe – Department of Applied Chemistry and Biochemical Engineering, Graduate School of Engineering, Shizuoka University, Hamamatsu, Shizuoka (Japan) *Powerful CO_2 methanation system by electrically heating spiral-type structured catalyst* Ryo Watanabe, Kohki Nishide, Hiroshi Akama, Choji Fukuhara Department of Applied Chemistry and Biochemical Engineering, Graduate School of Engineering, Shizuoka University, 3-5-1 Johoku, Chuo-ku, Hamamatsu, Shizuoka, Japan
16:00 – 16:20	OR74	Angelina Barthelmeß – KIT, Eggenstein-Leopoldshafen (Germany) *Enhancing CO_2 Hydrogenation Efficiency through in situ Formation of Active Species in Carbon Nitride Modified Catalysts* Angelina Barthelmeß,1 Dan Zhao,1 Maik Kahnt,2 Michael Zimmermann,1 Enrico Tusini,1 Timo Van Roje,1 Cherie Hsu,1 Thomas Sheppard,1 Anna Zimina,1 JAN-Dierk Grunwaldt,1 Moritz Wolf1 1 Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen/Germany, 2 MAX IV Laboratory, Lund/Sweden
16:20 – 16:40	OR75	Nassima Berroug – Chemical Technologies for Environmental Sustainability Group, Department of Chemical Engineering, Faculty of Science and Technology, University of the Basque Country, Bilbao (Spain) *Nickel acetylacetonate grafted on CaO-modified hydroxyapatite catalysts for enhanced performance in decarbonization processes: Effect of Ni loading* Nassima Berroug, Miguel A. Gutiérrez-Ortiz, Juan R. González-Velasco, Zouhair Boukha Chemical Technologies for Environmental Sustainability Group, Department of Chemical Engineering, Faculty of Science and Technology, University of the Basque Country UPV/EHU, P.O. Box 644, E-48080, Bilbao, Spain
16:40 – 17:00	Coffee-Break	
17:00 – 17:20	OR76	Catia Cannilla – Institute of Advanced Technology for Energy CNR-ITAE, Messina (Italy) *Effect of the pre-activation conditions on the nature of the active sites generated during CO_2 hydrogenation to MeOH over Cu-based catalysts* Catia Cannilla1, Mariarita Santoro1, Serena Todaro 1, Hanna Solt 2, Ferenc Lonyi 2, Francesco Arena 1, Giuseppe Bonura 1 1 Institute of Advanced Technology for Energy CNR-ITAE, S. Lucia sopra Contesse, 5, 98126 Messina, Italy. 2 Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Magyar tudósok körútja 2, H-1117, Budapest, Hungary.
17:20 – 17:40	OR77	Giuliano Giambastiani – University of Florence, Dept. of Chemistry "U. Schiff" DICUS, Sesto Fiorentino (Italy) *A Phoenix-like Covalent Triazine Framework as a Selective CO_2-to-Formate Electro-catalyst* Giuliano Giambastiani,1,2 Giulia Tuci,2 Andrea Rossin,2 Claudio Evangelisti,3 Giovanni Valenti,4 Francesco Paolucci,4 Yuefeng Liu5 1 University of Florence, Dept. of Chemistry "U. Schiff" DICUS, Via della Lastruccia 13, Sesto Fiorentino, Italy. 2 Institute of Chemistry of OrganoMetallic Compounds, ICCOM-CNR and Consorzio INSTM, Via Madonna del Piano, 10 - 50019, Sesto Fiorentino, Florence, Italy. 3 Institute of Chemistry of OrganoMetallic Compounds, ICCOM-CNR, Via G. Moruzzi 1 – 56124, Pisa, Italy. 4 Department of Chemistry "Giacomo Ciamician", University of Bologna, 40126 Bologna, Italy. 5 Dalian National Laboratory for Clean Energy (DNL), Dalian Institute of Chemical
17:40 – 18:00	OR78	Hsin Yu Chen – National Tsing Hua University, Department of Materials Science and Engineering, Hsinchu (Taiwan) *Atomic-scale insights into nanostructured MgO for thermocatalytic CO_2-to-CO conversion*

		Hsin-Yu Chen1,2, Shih-Yuan Chen3, Cheng-Hsi Yeh2, Chien-Neng Liao1,4, and Hsin-Yi Tiffany Chen1,2,4 1National Tsing Hua University, Department of Materials Science and Engineering, Hsinchu 300044, Taiwan. 2National Tsing Hua University, Department of Engineering and Systems Science, Hsinchu 300044, Taiwan. 3National Institute of Advanced Industrial Science and Technology (AIST), Energy Catalyst Technology Group, Energy Process Research Institute (EPRI), 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan. 4College of Semiconductor Research, National Tsing Hua University, Hsinchu 300044, Taiwan.
		Short Orals
18:00 – 18:10	SO75	Luciano Atzori – University of Cagliari, Department of Chemical and Geological Sciences, Monserrato (Italy) *Mesoporous Ni/ZrO_2-SiO_2 catalysts for the Dry Reforming of Methane* Luciano Atzori,1,2, Daniela Meloni1, Elisabetta Rombi1,2, M. Giorgia Cutrufello1,2 1 University of Cagliari,Department of Chemical and Geological Sciences, Monserrato (CA), Italy. 2 National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence, Italy.
18:10 – 18:20	SO76	Jung-Sik Kim – University of Seoul, Department of Materials Science and Engineering, Seoul (Republic of Korea) *Enhanced Photocatalytic Performance of (TiO_2-WO_3) Supported on $Sr_4Al_{14}O_{25}$:Eu, Dy under Visible Light* Hyun-sung KANG, Jung-Sik KIM The University of Seoul, Department of Materials Science and Engineering, Seoul 02504, Republic of Korea
18:20 – 18:30	SO77	Neha Choudhary – Institut Jean Le Rond D'Alembert, Sorbonne Université, CNRS UMR 7190, Saint-Cyr-L'Ecole (France) *Ni nanoparticles decorated over Y^{3+} promoted CeO_2 single-atom catalysts for enhanced low-temperature CO_2 methanation* Neha Choudhary1, Navdeep Srivastava2, Biplab Ghosh3, Patrick Da Costa1 1 Institut Jean Le Rond D'Alembert, Sorbonne Université, CNRS UMR 7190, 2 Place de la Gare de Ceinture, 78210 Saint-Cyr-L'Ecole, France 2 Department of Chemistry, Indian Institute of Technology-Indore, Simrol, Khandwa
18:30 – 18:40	SO78	Maria Córdoba Rodríguez – Technologies for Environmental Sustainability Group, Department of Chemical Engineering, Faculty of Science and Technology, University of The Basque Country UPV/EHU, Bizkaia (Spain) *Novel bimetallic La-Ni and Ba-Ni ceramic foams for dry reforming of methane* María Córdoba1, Andoni Choya1, Beatriz De Rivas1, Jose Ignacio Gutiérrez-Ortiz1, Rubén López-Fonseca1 1Technologies for Environmental Sustainability Group, Department of Chemical Engineering, Faculty of Science and Technology, University of The Basque Country UPV/EHU, Barrio Sarriena s/n, Leioa, Bizkaia E-48940, Spain.
18:40 – 18:50	SO79	Shafiq Falak – University of Milano-Bicocca, Dept. of Materials Science, Milano (Italy) *Design of nanostructured Cu oxides for the electrocatalytic CO_2 reduction* Falak Shafiq,1 Davide Melotto1, Tatiana Rodriguez-Flores1, Laura Vigni2, Mariangela Longhi2, Marco Montalbano2, Maria Vittoria Dozzi2, Lorenzo Mino3, Roberto Nistico'1 1 University of Milano-Bicocca, Dept. of Materials Science, Via R. Cozzi 55, Milano, Italy. 2 University of Milano, Dept. of Chemistry, Via C. Golgi 19, Milano, Italy. 3 University of Torino, Dept. of Chemistry and NIS Centre, Via P. Giuria 7, Torino, Italy.
18:50 – 19:00	SO80	Carlo Giorgio Visconti – Dipartimento di Energia, POLIMI, Milano, (Italy) *Unravelling S Poisoning Effects on Ru/Al_2O_3 CO_2 Methanation Catalysts Through in-situ and ex-situ Approaches* Clara Larghi1, Alessandro Porta1, Carlo Giorgio Visconti1, János Szanyi2, Luca Lietti1

		1 Dipartimento di Energia, Politecnico Di Milano, Milano, 20156, Italy 2 Institute for Integrated Catalysis, Pacific Northwest National Laboratory, Richland, 99352, WA, USA

04/06/2025		
Room ISOLA - RI		
10:00 – 10:20	OR79	withdrawn (substituted to OR19)
10:20 – 10:40	OR80	Juan Jose Villora Pico – School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast (UK) Enhanced CO_2 Hydrogenation to Hydrocarbons via SIL-Modified Fe-Ru/Al_2O_3 Catalysts: Tailoring Activity and Selectivity Through Support Engineering Juan José Villora-Picó1, Marina Maddaloni2, Ander Centeno-Pedrazo1, Jillian Thompson1, Chunfei Wu1, Nancy Artioli2, and Haresh Manyar1, 1 School of Chemistry and Chemical Engineering, Queen's University Belfast, David-Keir Building, Stranmillis Road, Belfast, BT9 5AG, UK; 2 CEEP Laboratory, Department of Civil Engineering, Architecture, Territory, Environment and Mathematics, University of Brescia, via Branze 38, 25123 Brescia, Italy
10:40 – 11:00	OR81	Samir Bensaid – POLITO, Dept. of Applied Science and Technology, Turin (Italy) *Effect of pre-treatment conditions on Fe-based catalyst for e-fuel production via modified Fischer-Tropsch synthesis* Alessio Tauro1, Fabio Salomone1, Fabrizio Celoria1, Marco Armandi1, Luca Nodari2, Luca Romagnoletti3, Emanuele Felli4, Raffaele Pirone1, Samir Bensaid1, 1 Polytechnic of Turin, Dept. of Applied Science and Technology, Corso Duca degli Abruzzi 24, 10129 Turin, Italy. 2 Istituto di Chimica della Materia Condensata e di Tecnologie per l'Energia (ICMATE), Consiglio Nazionale delle Ricerche (CNR), C.so Stati Uniti 4, 35127 Padova, Italy. 3 API Raffineria di Ancona S.p.A., Via Flaminia 685, 60015 Falconara Marittima (AN), Italy. 4 Italiana Petroli S.p.A., Via Salaria 1322, 00138 Roma, Italy.
11:00 – 11:20	Coffee-Break	
11:20 – 11:40	OR82	Claudio Contreras Diaz – Pontificia Universidad Católica de Chile, Departamento de Ingeniería Química y Bioprocesos, Escuela de Ingeniería, Santiago (Chile) *Improving Nickel Catalyst Dispersion on Phenol Hydrodeoxygenation by Amine-Assisted Impregnation* Claudio Contreras-Díaz1,2, Cesar Pazo-Carballo3, Claudio Araya-Lopez1,2, C. Sepulveda4 and Néstor Escalona1,2,3 1 Pontificia Universidad Católica de Chile, Departamento de Ingeniería Química y Bioprocesos, Escuela de Ingeniería, Santiago, Chile. 2 Núcleo Milenio en Procesos Catalíticos hacia la Química Sustentable, Santiago, Chile. 3 Pontificia Universidad Católica de Chile, Departamento de Química Física, Facultad de Química y Farmacia, Santiago, Chile. 4 Universidad de Concepción, Facultad de Ciencias Químicas, Edmundo Larenas 129, Concepción, Chile.
11:40 – 12:00	OR83	Bezawit Zerihun Desalegn – Hanyang University, Department of Chemical Engineering, Seoul (South Korea) *Tuning Multifunctionality for the Co-production of H_2, Carboxylic Acids and Electricity in a Multi-purpose Biomass-Fuel Cell* Bezawit Z. Desalegn, and Jeong Gil Seo Hanyang University, Department of Chemical Engineering, 04763, Seoul, South Korea. Hanyang University, Clean-Energy Research Institute, 04763, Seoul, South Korea.
12:00 – 12:20	OR84	Valérie Meille – IRCELYON, CNRS, UCBL, Villeurbanne (France) *Hydrogen release from perhydrobenzyltoluene: role of the catalyst support* Nataliia Marchenko, Mohamad Kharma, Franck Morfin, Laurent Piccolo, Nuno Rocha Batalha, Valérie Meille IRCELYON, CNRS, UCBL, 69100 Villeurbanne, France.

12:20 – 13:00	KN9	Andrzej Adamski – Jagiellonian University, Faculty of Chemistry, Kraków (Poland) *Cenosphere-based catalysts active in selected heterogeneous pro-environmental redox reactions* Paweł Rybowicz1, Yana Vitushynska1, Allison Proszowska1,2, Tomasz Polczyk1, Bogdan Samojeden3, Agata Łamacz4, Monika Motak3, Marek Michalik4, Andrzej Adamski,1 1 Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, 30-387 Kraków, Poland. 2 Jagiellonian University, Faculty of Biology, Gronostajowa 7, 30-387 Kraków, Poland. 3 AGH University of Krakow, Faculty of Energy and Fuels, Mickiewicza Ave. 30, 30-059 Kraków, Poland. 4 Wroclaw University of Technology, Faculty of Chemistry, Gdanska 7/9, 50-344 Wroclaw, Poland.
13:00 – 15:00	Lunch break	
		Short Orals
15:00 – 15:10	SO81	Chiara Aliotta – CNR, ISMN, Palermo (Italy) *Low-critical elements perovskite oxides for clean energy production and CO2 conversion* Chiara Aliotta1, Francesca Deganello1, Valeria La Parola1, Laura Valentino1, Eleonora La Greca1 and Leonarda Francesca Liotta1 1 CNR, ISMN, Via Ugo La Malfa 153, 90146-Palermo, Italy
15:10 – 15:20	SO82	Luca Cosentino – ISMN-CNR, Palermo (Italy) *Ni-La Perovskite Catalysts for CO_2 Methanation: Uncovering the Structure-Function Correlation* Luca Consentino,1,2, Miriam González-Castaño3, Luis F. Bobadilla3, Michelangelo Gruttadauria2, Leonarda Francesca Liotta1, José Antonio Odriozola3 1 ISMN-CNR, Via U. La Malfa 153, 900146 Palermo, Italy 2 STEBICEF Department Ed. 17, University of Palermo, Viale delle Scienze, 90128 Palermo, Italy 3 Department of Inorganic Chemistry, University of Seville (ICMS-CSIC), C/Americo Vespucio 49, 41092 Seville, Spain
15:20 – 15:30	SO83	Sven Kureti – Institute of Energy Process Engineering and Chemical Engineering, Chair of Reaction Engineering, TU Freiberg, Freiberg (Germany) *Transient isotopic study of low-temperature NOx reduction by H_2 on Pt/Mo/ZrO_2 catalyst* Daniel Schröder1, Sven Kureti1, 1Institute of Energy Process Engineering and Chemical Engineering, Chair of Reaction Engineering, TU Freiberg, Fuchsmuehlenweg 9D, 09599 Freiberg, Germany
15:30 – 15:40	SO84	Andrea Felli – Politechnical Department, University of Udine, Udine (Italy) *A Parametric Study on Ru-CeO_2 Catalysts for H_2 Production from NH_3 Decomposition* Andrea FELLI1, Maila DANIELIS1, Alessandro TROVARELLI1, Sara COLUSSI1 1Politechnical Department, University of Udine, Via del Cotonificio 108, 33100, Udine, IT
		Orals
15:40 – 16:00	OR85	Izabela Kurzydym – Faculty of Chemistry, Biological and Chemical Research Centre, University of Warsaw, Warszaw (Poland) *Overview of ZSM-5, CLI, and FAU catalysts with metallic dimers (Cu, Fe, Zn) and their sensitivity to poisoning by sulfur dioxide (SO_2) in the DeNOx process.* Izabela Kurzydym1, Izabela Czekaj2 1Faculty of Chemistry, Biological and Chemical Research Centre, University of Warsaw, ul. Żwirki i Wigury 101, 02-089 Warszaw, Poland 2Department of Organic Chemistry and Technology, Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 31-155 Cracow, Poland
16:00 – 16:20	OR86	Jean-François Lamonier – Unité de Catalyse et Chimie du Solide (UCCS), Univ. Lille, CNRS, Centrale Lille, Univ. Artois, Lille (France) *Promoting the efficient oxidation of toluene via non-thermal plasma-assisted synthesis of supported cobalt oxide catalysts* Victor Deboos1,2, Savita Kaliya Perumal Veerapandian2, Eliane Ghossein1,2, Jean-Marc Giraudon1, Rino Morent2, Nathalie De Geyter2, Jean-François Lamonier,1

		1Unité de Catalyse et Chimie du Solide (UCCS), Univ. Lille, CNRS, Centrale Lille, Univ. Artois, 59000 Lille, France 2 Unit Plasma Technology (RUPT), Department of Applied Physics Faculty of Engineering and Architecture, Ghent University, 9000 Ghent, Belgium
16:20 – 16:40	OR87	Luciana Lisi – Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili (STEMS) – CNR, Napoli (Italy) *NOx emission control by H_2-SCR over Pt-ZSM5 catalyst in mobile applications* Elisabetta M. Cepollaro1, Stefano Cimino1, Michele E. Fortunato1, Luciana Lisi,1 1Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili (STEMS) – CNR, P.le Tecchio 80 – 80125 Napoli, Italy
16:40 – 17:00	Coffee-Break	
17:00 - 17:20	OR88	Francesco Montanari – University of Florence, Department of Chemistry "Ugo Schiff", Sesto Fiorentino (Italy) *Effective upcycling of Pd(II) waste into an atomically precise Pd(II)-based catalyst for alkaline fuel cells applications* Francesco Montanari1, Marco Bonechi1,2, Carlotta Cappanni1, Pietro Gentilesca1, Matteo Savastano2,3, Mirko Severi1, Antonio Bianchi1,2, Massimo Innocenti1,2 1University of Florence, Department of Chemistry "Ugo Schiff", Via della Lastruccia 3-13, 50019 Sesto Fiorentino, Italy. 2 National Interuniversity Consortium of Material Science and Technology (INSTM), via G.Giusti 9, 50121, Italy. 3University San Raffaele Roma, Department of Human Sciences for the Promotion of Quality of Life, Via di Val Cannuta 247, 00166 Rome, Italy.
17:20 – 17:40	OR89	Tofik Nagiev – Nagiev Institute of Catalysis and Inorganic Chemistry of Ministry of Science and Education, Baku (Azerbaijan) *Gas-phase selective dehydrodimerization of 3-picoline In the coherent synchronization mode* Nagieva I.T.2, Malikova N.N.1, Ali-zadeh N.I.1, Nagiev T.M.1 1Nagiev Institute of Catalysis and Inorganic Chemistry of Ministry of Science and Education, Baku, Azerbaijan; 2Baku State University, Baku, Azerbaijan
17:40 – 18:00	OR90 exchange with OR101	Ying Zheng – Western University, Dept. of Chemical and Biochemical Engineering London, Ontario (Canada) *Plasma-Driven Modulation of Metal-Organic Frameworks for CO_2 hydrogenation* Nan Zou, Ying Zheng Western University, Dept. of Chemical and Biochemical Engineering London, Ontario, Canada
		Short Orals
18:00 – 18:10	SO85	Bernardo Patella – University of Palermo, Department of Engineering, Palermo, (Italy) *Fabrication of thermally annealed NiFeS ternary alloy for green hydrogen production* Bernardo Patella1, Salvatore Geraci1, Roberto Luigi Oliveri1, Nadia Moukri1, Giuseppe Aiello1, Filippo Pellitteri1, Cinzia Muriana1, Rosario Miceli1, Rosalinda Inguanta1 1University of Palermo, Department of Engineering, Viale delle Scienze, Palermo, Italy
18:10 – 18:20	SO86	Marta Stucchi – University of Milano, Chemistry Department, Milano (Italy) *Innovative materials for CO_2 capture and conversion to e-fuels* Marta Stucchi,1, Valentina Colombo1, Alessia Colombo1, Alberto Vertova1, Claudio Ampelli2, Siglinda Perathoner1. 1University of Milano, Chemistry Department, Via Golgi 19, 20133 Milano, Italy. 2 University of Messina, Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, Viale Ferdinando Stagno d'Alcontres 31, 98166 Messina, Italy.
18:20 – 18:30	SO87	Fabio Salomone – University of Calabria, Dept. of Environmental Engineering, Rende (Italy) *Hierarchical zeolites for methanol and dimethyl ether dehydration into light olefins* Emanuele Giglio,1, Giorgia Ferrarelli1, Fabio Salomone2, Elena Corrao3, Raffaele Pirone2, Samir Bensaid2, Massimo Migliori1, Girolamo Giordano1 1 University of Calabria, Dept. of Environmental Engineering, Via Pietro Bucci 45A, 87036 Rende (CS), Italy.

		2 Polytechnic of Turin, Dept. of Applied Science and Technology, Corso Duca degli Abruzzi 24, 10129 Turin, Italy. 3 University of Turin, Dept. of Chemistry, Via Pietro Giuria 7, 10125 Turin, Italy.
18:30 – 18:40	SO88	Shigeo Satokawa – Seikei University, Faculty of Science and Technology, Tokyo (Japan) *CO_2 hydrogenation activity over iron carbide catalysts having different crystal structures derived from iron oxalate* Akihide Yanagita, Daisuke Komizu, Haruki Horikoshi, Keigo Tashiro, Shigeo Satokawa Seikei University, Faculty of Science and Technology, 3-3-1 Kichijoji-kitamachi, Musashino-shi, Tokyo 180-8633, Japan.
18:40 – 18:50	SO89	Shaohua She – Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Tokyo (Japan) *Effect of Sulfonation Conditions on Performance of Sulfonated Lignin-Based Porous Carbon Catalyst* Shaohua She, Shunpei Takada, Kenji Kamiya, Eika W. Qian Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Nakacho, Koganei, Tokyo 184-8588, Japan
18:50 – 19:00	SO90	Michela Signoretto – Ca' Foscari University, Department of Molecular Sciences and Nanosystems, Venice (Italy) *Hydrodeoxygenation of isoeugenol catalyzed by Co/biochar catalyst* Lilia Longo1, Davide Baldassin1, Päivi Mäki-Arvela2, Joan Wärnå2, Mark E. Martinez Klimov2, Olha Yevdokimova2, Kari Eränen2, Dmitry Y. Murzin2, Michela Signoretto1. 1 Ca' Foscari University, Department of Molecular Sciences and Nanosystems, Venice, Italy. 2Åbo Akademi University, Johan Gadolin Process Chemistry Centre, Henriksgatan 2, 20500 Turku/Åbo, Finland

05/06/2025		
Room PR - Plenary		
08:50 – 09:30	KP2	Chemistry Europe Lecturer Annemie Bogaerts – Research group PLASMANT, Department of Chemistry - University of Antwerp, Campus Drie Eiken, Wilrijk-Antwerp, Belgium *Plasma catalysis: Complex chemical and physical mechanisms*
09:40 – 10:00	OR91	Patrick Da Costa – Sorbonne Université, Institut Jean Le Rond d'Alembert, CNRS UMR 7190, Saint-Cyr-L'Ecole (France) *On the structure reactivity and synthesis strategy of mixed-oxides prepared by microwave-assisted solution combustion synthesis – XAS and XRD operando study* Paulina Summa1,2, Katarzyna Świrk Da Costa 3, Li Li 4, Magnus Rønning 3, Monika Motak 2, Marta Gajewska 5, Changwei Hu 4, Patrick Da Costa 1, 1 Sorbonne Université, Institute Jean Le Rond d'Alembert, CNRS UMR 7190, 2 pl. de la gare de ceinture, Saint-Cyr-L'Ecole, France 2 AGH University of Science and Technology, Faculty of Energy and Fuels, Al. A. Mickiewicza 30, Kraków, Poland 3 Norwegian University of Science and Technology, Department of Chemical Engineering, Sem Sælands vei 4,Trondheim, Norway 4 Sichuan University, Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Chengdu, PR China 5 AGH University of Science and Technology, Academic Centre for Materials and Nanotechnology, Al. A. Mickiewicza 30, Kraków, Poland
10:00 – 10:20	OR92	Oscar Furst – KIT, Institute for Chemical Technology and Polymer Chemistry, Karlsruhe (Germany) *Comparative assessment of power-to-methane technologies for sustainable synthetic natural gas production* Oscar Furst1, Daniel Schmider2, Julian Dailly2, Olaf Deutschmann,1

		1Karlsruhe Institute of Technology, Institute for Chemical Technology and Polymer Chemistry, Kaiserstraße 12, Karlsruhe, Germany. 2European Institute for Energy Research, Emmy-Noether-Straße 11, Karlsruhe, Germany.
10:20 – 10:40	OR93	Weijie Ji – Key Laboratory of Mesoscopic Chemistry, MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing (China) *Very efficient yet durable urea electrosynthesis via carbon dioxide and nitrate over the defect-rich In_2O_3 nanotube* Hongjun Fang, Chen-Han Kuo, Hongsheng Yang, Ze Wang, Xinzhen Feng, Weijie Ji Key Laboratory of Mesoscopic Chemistry, MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China
10:40 – 11:00	OR94	Yanggeun Ju - School of Environment and Energy Engineering, Gwangju Institute of Science and Technology, Gwangju (Republic of Korea) *Enhancing Low-Temperature CO_2 Methanation: The Role of Praseodymium Oxide in Ni-Based Catalysts* Yanggeun, Junseo Park, Sung Bong Kang School of Environment and Energy Engineering, Gwangju Institute of Science and Technology, Gwangju, 61005, Republic of Korea
11:00 – 11:20	Coffee-Break	
		Short Orals
11:20 – 11:30	SO91	withdrawn
11:30 – 11:40	SO92	Renzo Leeflang – Wolfson Catalysis Centre, Department of Chemistry, University of Oxford, Oxford (UK) *Alkali Metal Promotion in Higher Alcohols and Olefin formation from CO_2 Hydrogenation: Shifting the Reaction Mechanism* Renzo A. Leeflang1, Sijie Huang1, Edman S.C. Tsang1, Guangchoa Li2 1 Wolfson Catalysis Centre, Department of Chemistry, University of Oxford, Oxford OX1 3QR, United Kingdom 2 Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hong Kong
11:40 – 11:50	SO93	Li Li – Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University (China) *Design of novel inverse ZrO_2/Ni catalysts for CO_2 utilization: from CO_2 to syn-methane* Li Li 1,2, Patrick Da Costa,2, Changwei Hu,1 1 Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, China. 2 Institut Jean Le Rond d'Alembert, Sorbonne Université, CNRS UMR 7190, 2 place de la gare de ceinture, Saint Cyr L'Ecole, France.
11:50 – 12:00	SO94	Luca Lietti – Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, Milan (Italy) *Storage element – catalyst interaction on different supports for cyclic CO_2 capture and methanation* Giuseppe Nava, Alessandro Porta, Roberto Matarrese, Carlo Giorgio Visconti, Luca Lietti1 Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano – Via La Masa 34, 20156 Milan, Italy
		Orals
12:00 – 12:20	OR123	Marco Etzi Coller Pascuzzi – Istituto Italiano di Tecnologia, Center for Sustainable Future Technologies, Torino (Italy) *Maximizing the efficiency of Ir-based oxygen evolution electrocatalysts through Ni doping* Anna Giulia Cardone1,2, Fabrizio Pirri1,2, Marco Etzi,1 1 Istituto Italiano di Tecnologia, Center for Sustainable Future Technologies, Via Livorno 60, 10144, Torino, Italy. 2 Politecnico di Torino, Dept. of Applied Science and Technology, Corso Duca degli Abruzzi 24, 10129, Torino, Italy.

12:20 – 12:40	OR124	Daniela Cozza – Chemical Engineering Catalysis and Sustainable Processes Laboratory, University of Calabria, Rende (Italy) *Catalytic methane cracking over amorphous and regular structured carbons* Enrico Catizzone, Daniela Cozza, Girolamo Giordano, Massimo Migliori, Chemical Engineering Catalysis and Sustainable Processes Laboratory, University of Calabria, Rende, Italy.
12:40 – 13:00	OR95	Matteo Guidotti – CNR-SCITEC, Milan (Italy) *Zirconia-based inorganic oxide catalysts for the abatement of highly toxic agrochemicals and chemical warfare agent simulants* Stefano Econdi1, Nicola Scotti1, Filippo Bossola1, Stefano Marchesi2, Chiara Bisio1,2, Fabio Carniato2, Matteo Guidotti1 1 CNR-SCITEC, via Golgi 19, Milan, Italy 2 DISIT, University of Eastern Piedmont "Amedeo Avogadro", via Michel 11, Alessandria, Italy
13.00 – 15:00	Lunch Break	
		Short Orals
15:00 – 15:10	SO95	Kristijan Lorber – National Institute of Chemistry, Ljubljana (Slovenia) *CO_2 activation dictates catalytic performance on different CeO_2 morphologies in the low temperature DRM reaction* Petar Djinović1,2, Kristijan Lorber,1 1 National Institute of Chemistry, Ljubljana, Slovenia. 2 University of Nova Gorica, Nova Gorica, Slovenia.
15:10 – 15:20	SO96	Shokouhallsadat Masoumilari – Department of Civil and Environment Engineering, University of Ulsan, Ulsan (Republic of Korea) *Dual-Function Bi-Based Electrodes for Coupled CO_2 Reduction and Glycerol Oxidation* Shokouh Masoumi, Zohreh Masoumi, Daeseung Kyung Department of Civil and Environment Engineering, University of Ulsan, Daehakro 93, Namgu, Ulsan 44610, Republic of Korea
15:20 – 15:30	SO97	Federica Orabona – Åbo Akademi, Laboratory of Industrial Chemistry and Reaction Engineering (TKR), Turku/Åbo (Finland) *CO_2 cycloaddition to limonene diepoxide: catalysis, kinetics and mass transfer* Federica Orabona,1,2, Stefano Napolitano1,2, Veronika D. Badazhkova2, Wander Perez-Sena2, Kari Eränen2, Martino Di Serio1, Dmitry Murzin2, Vincenzo Russo1,2, Tapio Salmi1,2 1 Università di Napoli 'Federico II', Chemical Sciences, IT-80125 Napoli, Italy 2 Åbo Akademi, Laboratory of Industrial Chemistry and Reaction Engineering (TKR), FI-20500 Turku/Åbo, Finland
15:30 – 15:40	SO98	Andrea Rizzetto – POLITO, Department of Applied Science and Technology (DISAT), Turin (Italy) *Low-content Ru catalysts for efficient atmospheric CO_2 methanation* Andrea Rizzetto, Marco Pietro Mezzapesa, Enrico Sartoretti, Fabio Salomone, Marco Piumetti, Raffaele Pirone, Samir Bensaid Politecnico di Torino, Department of Applied Science and Technology (DISAT), Corso Duca degli Abruzzi 24, 10129, Turin, Italy.
15:40 – 15:50	SO99	Matteo Maestri – Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, Milano (Italy) *Deciphering Effects of Nanoparticles Shape and Size on the Structure Sensitivity of the CO_2 Methanation Reaction on Ni* Gabriele Spano',1 Matteo Ferri,1 Raffaele Cheula,1 Matteo Monai,2 Bert M. Weckhuysen,2 Matteo Maestri1 1 Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, Via La Masa, 34, 20156, Milano, Italy. 2 Inorganic Chemistry and Catalysis Group, Institute for Circular and Sustainable Chemistry and Debye Institute for Nanomaterials Science, Utrecht University,
15:50 – 16:00	SO100	Paolo Squillaci – ChiBioFarAm – University of Messina, ERIC aisbl and CASPE/INSTM, Messina (Italy)

		Enhancing CO_2ER to ethylene over CuO electrodes by Ni and B modification Paolo Squillaci, G. Papanikolaou, P. Lanzafame, D. Chillè, S. Perathoner and G. Centi Department of Chemical, Biological, Pharmaceutical and Environmental Sciences (ChiBioFarAm) – University of Messina, ERIC aisbl and CASPE/INSTM, V.le F. Stagno d'Alcontres 31, 98166 Messina, Italy.
16:00 – 16:10	SO101	Alessio Tauro – POLITO, Dept. of Applied Science and Technology, Turin (Italy) *Effect of zeolite acidity on pre-treated Fe-based catalysts for e-fuel production via CO_2-modified Fischer-Tropsch Synthesis* Alessio Tauro1, Fabio Salomone,1, Fabrizio Celoria1, Luca Nodari2, Luca Romagnoletti3, Emanuele Felli4, Raffaele Pirone1, Samir Bensaid1 1 Polytechnic of Turin, Dept. of Applied Science and Technology, Corso Duca degli Abruzzi 24, 10129 Turin, Italy. 2 Istituto di Chimica della Materia Condensata e di Tecnologie per l'Energia (ICMATE), Consiglio Nazionale delle Ricerche (CNR), C.so Stati Uniti 4, 35127 Padova, Italy. 3 API Raffineria di Ancona S.p.A., Via Flaminia 685, 60015 Falconara Marittima (AN), Italy. 4 Italiana Petroli S.p.A., Via Salaria 1322, 00138 Roma, Italy.
16:10 – 16:20	SO102	Luca Lietti – Laboratory of Catalysis and Catalytic Processes, Department of Energy Politecnico di Milano, Milano (Italy) *Promoted Fe catalyst for direct conversion of CO_2 into e-crude* Mattia Piacentini1, Beda Rolandi1, Alessandro Porta1, Luca Lietti1, Carlo Giorgio Visconti1 Laboratory of Catalysis and Catalytic Processes, Department of Energy Politecnico di Milano, via La Masa 34, 20156, Milano ITALY
16:20 – 16:30	SO103	withdrawn
16:30 – 16:40	SO104	Kinga Mlekodaj – J. Heyrovský Institute of Physical Chemistry of the CAS, Prague (Czech Republic) *Effective upgrade of CO_2 and CH_4 to high-value products over iron-containing Al-rich BEA zeolite* Kinga Mlekodaj1, Kinga Gora-Marek,2, Karolina Tarach2, Julia Sobalska 2,3, Agnieszka Kornas1, Radim Pilar1, Dalibor Kaucky1, Edyta Tabor,1 1 J. Heyrovský Institute of Physical Chemistry of the CAS, v. v. i., Dolejškova 2155/3, 182 23 Prague 8, Czech Republic. 2 Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Kraków, Poland. 3 Doctoral School of Exact and Natural Sciences, Jagiellonian University in Krakow, Łojasiewicza 11, 30-348 Krakow, Poland.
16:40 – 17:00	Coffee-Break	
17:00 – 17:20	OR96	withdrawn
17:20 – 17:40	OR97	withdrawn
17:40 – 18:00	OR98	Hidenori Yahiro – Graduate School of Science and Engineering, Ehime University, (Japan) *Low Temperature-Water Gas Shift Reaction Using Perovskite-type Oxide Catalyst Containing Cerium Ion* Hidenori Yahiro1, Noa Yamaguchi1, Satoshi Toshioka1, Hiroyuki Yamaura1, Syuhei Yamaguchi1, Anna Paola Panunzi2, Leonardo Duranti2, Elisabetta Di Bartolomeo2 1 Graduate School of Science and Engineering, Ehime University, Matsuyama 790-8577, Japan 2 Department of Chemical Sciences and Technologies, University of Rome Tor Vergata, via della Ricerca Scientifica, 00133 Rome, Italy
18:00 – 18:20	OR99	Bin Feng - State Key Laboratory of High-Temperature Gas Dynamics, Institute of Mechanics, Chinese Academy of Sciences, Beijing (China) *Oxygen migration and oxidation pathway for soot oxidation in presence of NO by two-step isotope experiment* Zirui Zhang1,2, Cen Sun1,2, Xiaolin Wei1,2, Shaohua Wu3, Gehan A J Amaratunga4, Feng Bin1,2, Wenjun Liang5

		1 State Key Laboratory of High-Temperature Gas Dynamics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China; 2 School of Engineering Science, University of Chinese Academy of Sciences, Beijing 100049, China; 3 Dalian University of Technology, Dalian 116000, PR China; 4 Department of Engineering, University of Cambridge, CB3 0FA, Cambridge, United Kingdom; 5 Key Laboratory of Beijing on Regional Air Pollution Control, Beijing University of Technology, Beijing 100124, PR China.
18:20 – 18:40	OR100	Nicoletta Rusta – University of Cagliari, Department of Chemical and Geological Sciences, Cagliari (Italy) *Design of Ceria-based Catalysts via Self-Combustion Approaches for CO_2 Conversion to Dimethyl Carbonate* Nicoletta RUSTA1,2, Valentina Mameli1,2, Stefania Porcu2,3, Aryane A. Marciniak4, Evelyn C. S. Santos5, Odivaldo Cambraia Alves 6, Claudio J. A. Mota4,5,7, Elisabetta Rombi1,2, Carla Cannas1,2 1 University of Cagliari, Department of Chemical and Geological Sciences, Cagliari, Italy. 2 National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence, Italy. 3 University of Cagliari, Department of Physics, , Cagliari, Italy. 4 Universidade Federal do Rio de Janeiro, Escola de Química, Rio de Janeiro, Brasil 5 Universidade Federal do Rio de Janeiro, Instituto de Química, Rio de Janeiro, Brasil 6 Universidade Federal Fluminense, Instituto de Química, Niterói, Brazil 7 INCT Energia & Ambiente, UFRJ, Brazil
		Short Orals
18:40 - 18:50	SO133	Fausto Secci – Department of Chemical and Geological Sciences, University of Cagliari, Monserrato (Italy) *Confined growth of ultrasmall NiO nanoparticles into mesostructured and mesoporous SiO_2, γ-Al_2O_3 and CeO_2 supports for CO_2 methanation* Fausto Secci1,2, Nicoletta Rusta1,2, Luciano Atzori1,2, Maria Giorgia Cutrufello1,2, Daniela Meloni1, Carla Cannas1,2, Elisabetta Rombi1,2 1 Department of Chemical and Geological Sciences, University of Cagliari, Monserrato (CA), Italy 2 National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence, Italy
18:50 – 19:00	SO134	L. Valentino, Institute for the Study of Nanostructured Materials (ISMN), Palermo, Italy *Optimizing Ni-Based Catalysts for Dry Reforming of Methane: Impact of MgO Supports Doped with Fe, Cu, and Ce* L. Valentino,1, G. Pantaleo1, V. La Parola1, A. Giroir-Fendler2, L.F. Liotta1 1 Institute for the Study of Nanostructured Materials (ISMN), National Research Council (CNR), Via Ugo La Malfa 153, 90146 Palermo, Italy 2 Universite Claude Bernard Lyon 1, IRCELYON, UMR 5256 CNRS, 43 Boulevard du 11 Novembre 1918, Villeurbanne 69622, France.
19:00 – 19:10	SO135	Chiara Negri – Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, Milano (Italy) *A combined operando UV-vis and flow reactor study of the NH3-SCR redox kinetics over Cu-CHA* C. Negri1, N. Usberti1, G. Contaldo1, M. Bracconi1, I. Nova1, M. Maestri1, E. Tronconi1 Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, 20156 Milano (Italy)
19:10 – 19:20	SO136	withdrawn
19:20 – 19:30	Closing	

05/06/2025		
Room Massimo - RM		
09:40 – 10:00	OR101	shifted to OR90
10:00 – 10:20	OR102	Camilla Monacciani – POLITO, Department of Applied Science and Technology (DISAT), Turin (Italy) *TiO_2 on Gold Nanostars Enhances Photocatalytic Water Reduction in the Near Infrared Regime* Camilla Monacciani, Debora Ferrari, Tiziano Dainese, Chiara Deriu, and Laura Fabris Polythecnic of Turin, Department of Applied Science and Technology (DISAT), Corso Duca degli Abruzzi 24, Turin, Italy
10:20 – 11:00	KN4	Jerome Canivet – Université Claude Bernard Lyon 1, CNRS, IRCELYON - UMR 5256, Villeurbanne (France) *Porous Macroligands for Heterogenized Photocatalytic Solar Fuel Production* Jérôme Canivet, Emilien Chaigne--Tarlotin, Elsje Alessandra Quadrelli Université Claude Bernard Lyon 1, CNRS, IRCELYON - UMR 5256, 2 Avenue Albert Einstein, 69626 Villeurbanne Cedex, France
11:00 – 11:20	Coffee-Break	
		Short Orals
11:20 – 11:30	SO105	Ahmed Ragab Saleh Belmashkan – ChiBioFarAm, University of Messina, ERIC aisbl and INSTM/CASPE, Messina (Italy) *Electrification by Induction Heating for Sustainable Dehydrogenation of Ethylbenzene to Styrene* Ahmed Ragab Saleh Belmashkan,1 Gianfranco Giorgianni1, Vahideh Abbassi1, Siglinda Perathoner1, Gabriele Centi1, Angelo Ferrando2, Gianni Marchetti2, Salvatore Abate1 1 Department of ChiBioFarAm (Industrial Chemistry), University of Messina, ERIC aisbl and INSTM/CASPE, V.le F. Stagno d'Alcontres 31, Messina 98166, Italy 2 Basic Chemical & Plastics Research Centre Versalis - Stabilimento di Mantova Via Taliercio 14, 46100 Mantova, Italy
11:30 – 11:40	SO106	Donatella Chillé – ChiBioFarAm, University of Messina, ERIC a.i.s.b.l. and CASPE/INSTM, Messina (Italy) *Modification of Ordered Mesoporous Carbon materials for Enhancing the Electrocatalytic Oxidation of Phenol to p-benzoquinone* Donatella Chillé, Paolo Squillaci, Georgia Papanikolaou, Siglinda Perathoner, Gabriele Centi and Paola Lanzafame Department of Chemical, Biological, Pharmaceutical and Environmental Sciences (ChiBioFarAm), University of Messina, ERIC a.i.s.b.l. and CASPE/INSTM, V.le F. Stagno d'Alcontres 31, 98166 Messina, Italy
11:40 – 11:50	SO107	Mario Samperi – Institute of Advanced Techn. for Energy CNR-ITAE, Messina (Italy) *Unveiling the deactivation process of Amberlyst-15 in the etherification reaction of glycerol with ethanol* Mario Samperi1, Giuseppe Bonura1, Mariarita Santoro1, Serena Todaro1, Alessandro Cajumi2, Mauro Failla1, Francesco Arena2, Catia Cannilla1 1 Institute of Advanced Technology for Energy CNR-ITAE, S. Lucia sopra Contesse 5, 98126 Messina, Italy. 2 University of Messina, Dept. of Engineering, c.da Papardo, 98166 Messina, Italy.
11:50 – 12:00	SO108	Stefano Savino – ICCOM-CNR, SS Bari, Bari, Italy. *Steel slag as a highly efficient catalyst for hydrodeoxygenation of fatty acids: from a residue to a precious material for renewable fuels production* Stefano Savino1, Giuseppe Guglielmo2, Rosella Attrotto2, Elena Ghedini3, Michele Casiello1, Fiorenza Fanelli1, Lucia D'accolti1,3, Angelo Nacci1,3 1 ICCOM-CNR, SS Bari, Via Orabona 4, 70126 Bari, Italy. 2 Research and Development Department, Acciaierie d'Italia S.p.A., SS Appia km 648, 74123 Taranto, Italy. 3 Chemistry Department, Università degli Studi di Bari Aldo Moro, 70125 Bari, Italy.
		Orals

12:00 – 12:20	OR103	Michele Bigica – Dipartimento di Chimica, Università degli Studi di Milano, Milano (Italy) *Innovative metal functionalized hydroxyapatite/carbon nitride nanocomposite material to enhance CO_2 electroreduction to formate* Michele Bigica,1 Sebastiano Campisi,1 Antonella Gervasini,1 Pierangela Cristani,2 Andrei Khodakov,3 Vitaly Ordomsky3 1 Dipartimento di Chimica, Università degli Studi di Milano, 20133 Milano, Italy 2 Ricerca sul Sistema Energetico - RSE S.p.A., 20134 Milano, Italy 3 CNRS-UCCS, 59650 Villeneuve d'Ascq Cedex, France
12:20 – 12:40	OR104	Antoinette Maarawi Chidraoui – Univ Grenoble Alpes, CEA, Liten, DTCH, Laboratoire Réacteurs et Procédés (LRP), Grenoble (France) *Direct hydrogenation of CO_2 into liquid hydrocarbons: kinetics and reactor design* Antoinette Maarawi Chidraoui, Carlotta Panzone, Alban Chappaz, Geneviève Geffraye, Albin Chaise Univ Grenoble Alpes, CEA, Liten, DTCH, Laboratoire Réacteurs et Procédés (LRP), 38000 Grenoble, France.
12:40 – 13:00	OR105	Maria Rosaria Acocella – University of Salerno, Department of Chemistry and Biology "A Zambelli", Fisciano (Italy) *CO_2 Sorption Accelerated by Mechanical Grinding* Maria Rosaria Acocella 1, Aida Kiani,2 Katerina Kostantinova Charakova1 1University of Salerno, Department of Chemistry and Biology "A Zambelli", Via Giovanni Paolo II, 132-84080- Fisciano (Salerno) Italy
13:00 – 15:00		Lunch break
		Short Orals
15:00 – 15:10	SO109	Kosuke Watanabe - Waseda University, Department of Applied Chemistry, Shinjuku, Tokyo (Japan) *Oxidative dehydrogenation of ethane combined with CO_2 splitting via chemical looping technique utilising redox of In_2O_3* Kosuke Watanabe1, Takuma Higo1, Koki Saegusa1, Sakura Matsumoto1, Hiroshi Sampei1, Yuki Isono2, Akira Shimojuku2, Hideki Furusawa2, And Yasushi Sekine1 1Waseda University, Department of Applied Chemistry, Shinjuku, Tokyo 169-8555, Japan. 2JX Advanced Metals Corporation, Isohara Branch, Technology Develop Center, Kitaibaraki, Ibaraki 319-1535, Japan.
15:10 – 15:20	SO110	Lijiang Fan – Tokyo University of Agriculture and Technology, Tokyo (Japan) *Structurally Controllable Strong Acid Mesoporous Catalyst SBA-15-TESBS: Synthesis and Application in Biodiesel Production* Lijiang Fan, Eika Qian, Kenji Kamiya, Peng Mingming Tokyo University of Agriculture and Technology.
15:20 – 15:30	SO111	Juan Jose Villora-Pico – School of Chemistry and Chemical Engineering, Queen's University Belfast (UK). *Designing Holistic Biorefinery Solutions: Process Optimisation and Technoeconomic Viability of Glycerol derived High Energy-Density Fuel Additives* John Keogh, Manish Tiwari, Callum Jeffrey, Krutarth Pandit, and Haresh Manyar School of Chemistry and Chemical Engineering, Queen's University Belfast, David-Keir Building, Stranmillis Road, Belfast, BT9 5AG, UK.
15:30 – 15:40	SO112	Elham Nejadmoghadam, Chalmers University of Technology,Sweden. *Catalyst deactivation in green hydrotreaters: Impact of catalyst composition* Elham Nejadmoghadam,1 Olov Öhrman 2, Derek Creaser 1, Louise Olsson1 1 Chemistry and Chemical Engineering, Chalmers University of Technology, Gothenburg 41296, Sweden. 2 Preem AB, Gothenburg SE-418 23, Sweden
15:40 – 15:50	SO113	Emilia Paone – Dipartimento DICEAM, Università degli Studi Mediterranea di Reggio Calabria, (Italy) *Spent Lithium Cobalt Oxide Batteries: Heterogeneous Catalyst for Upcycling Lignocellulosic Biomass* Emilia Paone,1,2, Giulia Maria Itri1, Francesco Mauriello1

		1 Dipartimento DICEAM, Università degli Studi Mediterranea di Reggio Calabria, (Italy)
15:50 – 16:00	SO114	Rosalba Passalacqua – ChiBioFarAm & INSTM CASPE (Lab. of Catalysis for Sustainable Production & Energy, Messina (Italy) *Conversion of glucaric acid to adipic acid by Pd−ReOx catalyst supported on carbon-based materials* Rosalba Passalacqua1, Salvatore Abate1, Siglinda Perathoner1, Gabriele Centi1, Alfredo Aloise2, Cristiano Maesanii3, Claudia Castelli3, Stefano Alini3 1 University of Messina, Department of Chemical, Biological, Pharmaceutical and Environmental Sciences (ChiBioFarAm) & INSTM CASPE (Lab. of Catalysis for Sustainable Production & Energy, Viale F. Stagno d'Alcontres 31, 98166 Messina, Italy 2 Department of Physical and Chemical Sciences, University of L'Aquila, via Vetoio, Coppito 2 67100 L'Aquila, Italy 3 Radici Group, Via G. Fauser, 50, Novara 28100 - Italy
16:00 – 16:10	SO115	Marco Russo – Institute of Nanostructured Materials, ISMN-CNR, Palermo (Italy) *Sulfonated metal oxide catalysts for the cascade conversion of levulinic acid to isopropyl levulinate and γ-valerolactone* Marco Russo, Chiara Aliotta, Valeria La Parola, Giuseppe Pantaleo, Maria Luisa Testa Institute of Nanostructured Materials, ISMN-CNR, Via Ugo La Malfa 153, 90146 Palermo, Italy.
16:10 – 16:20	SO116	Giuseppe Salierno – University of Bologna, "Toso Montanari" Department of Industrial Chemistry, Bologna (Italy) *Model molecule investigation for the reductive catalytic fractionation of lignin using innovative magnetic catalysts* Federico Bugli1, Giuseppe Salierno1,2, Fabrizio Cavani1,3, Tommaso Tabanelli,1,3 1 University of Bologna, "Toso Montanari" Department of Industrial Chemistry, Via Piero Gobetti 85, 40129, Bologna, Italy. 2 University of Perugia, Department of Chemistry, Biology and Biotechnology, Via Elce di Sotto 8, 06132, Perugia, Italy. 3 University of Bologna, Center for Chemical Catalysis - C3, Via Piero Gobetti 85, 40129, Bologna, Italy.
16:20 – 16:30	SO117	withdrawn
16:30 – 16:40	SO118	Valérie Theuns – Univ. Lille, CNRS, UCCS – Unité de Catalyse et Chimie du Solide, Lille (France) *Exploring $BaTiO_3$-Derived Materials for Advancing SOFC Electrode Performance* Valerie Theuns1, Donovan Ledru2, Marie-Hélène Chambrier2, Aurélie Rolle1, Anne-Sophie Mamede1, Héloïse Tissot1, Elise Berrier1 1 Univ. Lille, CNRS, UCCS – Unité de Catalyse et Chimie du Solide, F-59000 Lille, France. 2 Univ. Artois, CNRS, Centrale Lille, Univ. Lille, UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, F62300 Lens, France
16:40 – 17:00	Coffee-Break	
17:00 – 17:20	OR106	Fabian H. Müller – Institute for Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen (Germany) *Integrated direct air capture and activation of CO_2 on metal-free covalent triazine frameworks* Fabian H. Müller1, Chalachew Mebrahtu1,2, Regina Palkovits1,2 1 Institute for Technical and Macromolecular Chemistry, RWTH Aachen University, Worringerweg 2, 52074 – Aachen, Germany. 2 Institute for Sustainable Hydrogen Economy, Forschungszentrum Jülich, Am Brainergy Park 1, 52428 – Jülich, Germany.
17:20 – 17:40	OR107	Maria Romay – Thermochemical Processes Unit, IMDEA Energy Institute, Madrid (Spain) *Dry Reforming of Biogas over $La_{0.9}Sr_{0.1}Fe_{0.95}Ni_{0.05}O_3$ Perovskite for Syngas Production* María Romay 1, David P. Serrano1,2, José.M Escola2, Patricia Pizarro,2 1 Thermochemical Processes Unit, IMDEA Energy Institute, Avda. Ramón de la Sagra 3, Móstoles, 28935 Madrid, Spain.

		2 Chemical and Environmental Engineering Group, Rey Juan Carlos University, c/ Tulipán s/n, Móstoles, 28933 Madrid, Spain.
17:40 – 18:00	OR108	Yasushi Sekine – Waseda University, Department of Applied Chemistry, Shinjuku, Tokyo, Japan. *Effective conversion of CO_2 at lower temperatures in an electric field* Yasushi Sekine,1 1Waseda University, Department of Applied Chemistry, Shinjuku, Tokyo, Japan.
18:00 – 18:20	OR109	Katarzyna Swirk Da Costa – 1Norwegian University of Science and Technology, Department of Chemical Engineering, Trondheim (Norway) *How to improve stability in excess-methane dry reforming over Ni/KIT-6 catalysts? Reduction behavior of thermally stable Ni phyllosilicates (Si/Ni=1:1) monitored by in situ/operando XAS-XRD and IR spectroscopy* Katarzyna Świrk Da Costa1, Paulina Summa2, Marco Fabbiani3, Magnus Rønning1 1Norwegian University of Science and Technology, Department of Chemical Engineering, 7491 Trondheim,Norway 2Sorbonne Université, CNRS, Institut Jean Le Rond d'Alembert, 78210 Saint Cyr l'Ecole, France 3Université de Caen, ENSICAEN, CNRS, Laboratoire Catalyse et Spectrochimie, 14000 Caen, France
18:20 – 18:40	OR110	Daniele Giusi – ChiBioFarAm – University of Messina, ERIC aisbl and CASPE/INSTM, Messina (Italy) *A scalable artificial leaf device with high solar-to-fuel efficiency to formate* Daniele Giusi,1, Veronica Costantino1, Viviana Amoroso1, Sefora Isabella Perricone1, Siglinda Perathoner1, Gabriele Centi1, Claudio Ampelli1 1 Department of Chemical, Biological, Pharmaceutical and Environmental Sciences (ChiBioFarAm) – University of Messina, ERIC aisbl and CASPE/INSTM, V.le F.Stagno d'Alcontres, 31 – 98166 Messina, Italy.
		Short Orals
18.40 – 18:50	SO137	Marco Pietro Mezzapesa – POLITO, Department of Applied Science and Technology (DISAT), Turin (Italy) *Spectroscopic investigation of In_2O_3-ZrO_2 catalyst for CO_2 hydrogenation to methanol* Marco Pietro Mezzapesa, Fabio Salomone, Enrico Sartoretti, Raffale Pirone, Samir Bensaid Politecnico di Torino, Department of Applied Science and Technology (DISAT), Corso Duca degli Abruzzi 24, 10129 Turin, Italy.
18:50 – 19:00	SO138	Nassar Nabil – University of Lille, CNRS, Centrale Lille, ENSCL, University of Artois, UMR 8181-UCCS- Unité de Catalyse et Chimie du Solide, Lille, France *ME-PSD IR spectroscopy to study CO Oxidation reaction under Pt/Al_2O_3 catalyst* Nassar N., Djaafri A., Richard M., Dujardin C., Tougerti A., Cristol S. University of Lille, CNRS, Centrale Lille, ENSCL, University of Artois, UMR 8181-UCCS- Unité de Catalyse et Chimie du Solide, F-59000 Lille, France
19:00 – 19:10	SO139	Enrico Tronconi – Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, Milan (Italy) *Low-Temperature redox kinetics for NH3-SCR and N2O formation over Cu-CHA catalysts* Nicola Usberti1, Andrea Gjetja1, Isabella Nova1, Enrico Tronconi,1 , Roberta Villamaina2, Maria Pia Ruggeri2, Djamela Bounechada2, Andrew P. E. York2, Jillian Collier2 1 Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, Via La Masa, 34, 20156 Milan, Italy 2 Johnson Matthey Technology Centre, Blounts Court Road, Sonning Common, Reading RG4 9NH, UK
19:10 – 19:20	SO140	Avelina Garcia Garcia – Grupo MCMA, Departamento de Química Inorgánica e Instituto Universitario de Materiales, Universidad de Alicante, San Vicente del Raspeig (Spain) *Unlocking NOx Reduction Pathways in CO-Assisted NO Reduction over Ultra-Low Metal Content Catalysts Supported on Ceria-Zirconia* J.C Martínez-Munuera1, R. Matarrese2, L. Castoldi2, L. Lietti2, A. García-García,1

		1Grupo MCMA, Departamento de Química Inorgánica e Instituto Universitario de Materiales, Universidad de Alicante, Carretera de San Vicente del Raspeig s/n, 03690 San Vicente del Raspeig, Spain. 2Gruppo di Catalisi e Processi Catalitici, Dipartimento di Energia, Politecnico di Milano, Via La Masa 34, 20156 Milano, Italy.
19:20 – 19:30	Closing	

05/06/2025		
Room Isola - RI		
09:40 – 10:00	OR111	Matthew Drewery – University of Newcastle, Chemical Engineering, University Drive, Callaghan (Australia) *Implementation of Catalytic Technologies for Mitigation of Humid, Lean Methane Exhaust Streams; Technological Hurdles for Industrial Implementation* Matthew Drewery1, Matthew Bligh1, Ryan Noon1, Luke Harvey1, Martin Hartmann2, Wilhelm Schwieger2, Eric M Kennedy1, Michael Stockenhuber1 1University of Newcastle, Chemical Engineering, University Drive, Callaghan, Australia. 2Friedrich Alexander Universität, Chemical and Bioengineering, Egerlandstr, Erlangen, Germany.
10:00 – 10:20	OR112	William Epling – University of Virginia, Charlottesville, VA, USA *Impact of NO_2 on Sulfur Poisoning of Cu-SSZ-13 Catalysts* Afrina Zaman Shoronika1, Poonam Rani1, Rohil Daya2, and William Epling1 1University of Virginia, Charlottesville, VA, USA 2Cummins Inc., Columbus, IN, USA
10:20 – 10:40	OR113	Nadia Grifasi – POLITO, Department of Applied Science and Technology, Turin (Italy) *Synergistic effect between manganese and copper oxides in boosting low-temperature catalytic oxidation of indoor pollutants* Nadia Grifasi, Giorgio Demichelis, Samir Bensaid, Nunzio Russo, Debora Fino, Marco Piumetti Polytechnic of Turin, Department of Applied Science and Technology, Corso Duca Degli Abruzzi, 24, 10129, Turin, Italy
10:40 – 11:00	OR114	Richard Knopp – University of Chemistry and Technology, Dept. of Chemical Engineering, Technická 5, Prague (Czech Republic) *Kinetics of site transformations in Pd/AEI zeolite for NOx adsorption* Petr Kočí,1, Tetyana Zheleznyak1, Richard Knopp1, Maria Pia Ruggeri2, Djamela Bounechada2, Andrew P.E. York2 1University of Chemistry and Technology, Dept. of Chemical Engineering, Technická 5, Prague, Czech Republic. 2Johnson Matthey Technology Centre, Blounts Court Road, Sonning Common, Reading, UK.
11:00 – 11:20	Coffee-Break	
		Short Orals
11:20 – 11.30	SO119	Luana De Pasquale – University of Messina, Dept. of Chemical, Biological, Pharmaceutical and Environmental Sciences, Messina (Italy) *Magnetic ferrite-based materials for hydrogen generation via water photo-electrolysis* Daniele Valenzisi1, Falak Shafiq1, Luana De Pasquale,2, Tatiana Rodriguez-Flores1, Roberto Nistico'1, Matteo Cantoni3, Marco Montalbano4, Maria Vittoria Dozzi4, Mery Malandrino5, Maria Cristina Paganini5, Chiara Genovese2 1 Univ. of Milano-Bicocca, Dept. of Materials Science, Via R. Cozzi 55, Milano, Italy. 2 University of Messina, Dept. of Chemical, Biological, Pharmaceutical and Environmental Sciences, Viale F.S. D'Alcontres 31, Messina, Italy. 3 Politecnico di Milano, Dept. of Physics, Via G. Colombo 81, Milano, Italy. 4 University of Milano, Dept. of Chemistry, Via C. Golgi 19, Milano, Italy. 5University of Torino, Dept. of Chemistry and NIS Centre, Via P. Giuria 7, Torino, Italy.
11:30 – 11:40	SO120	shifted to SO64
11:40 – 11:50	SO121	Kamila Sobańska – Faculty of Chemistry, Jagiellonian University, Kraków (Poland)

		Electroprotic reactions of hydrogen peroxide at the interface of aqueous solution and the surface of amorphous oxide ZrO2, Nb2O5, HfO2, Ta2O5 gels – relevance for advanced oxidation processes Kamila Sobańska,,1 Łukasz Wolski,2 Piotr Pietrzyk1 1Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, 30-387 Krakow, Poland. 2Adam Mickiewicz University, Faculty of Chemistry, Uniwersytetu Poznańskiego 8, 61-614 Poznań, Poland.
11:50 – 12:00	SO122	Jiaqiang Wang – Yunnan Provincial Center of Technology Innovation for New Materials and Equipment in Water Pollution Control, Yunnan University, Kunming (China) *The challenge of large-scale application of biomimetic photocatalytic water treatment* Jiaqiang Wang, Yi Zhao, Die Zou, Han Zhang, Chenjie Duan Yunnan Provincial Center of Technology Innovation for New Materials and Equipment in Water Pollution Control, School of Materials and Energy, School of Chemical Sciences & Technology, Yunnan Province Engineering Research Center of Photocatalytic Treatment of Industrial Wastewater, Yunnan University, Kunming, 650091, P. R. China
		Orals
12:00 – 12:20	OR115	Francesco Tavella – ChiBioFarAm – University of Messina, ERIC aisbl and CASPE/INSTM, Messina (Italy) *A novel gas-phase approach to control selectivity in ethanol photo-oxidation on metal-doped TiO_2/Ti gauze photoanodes* Francesco Tavella,1, Luana De Pasquale 1, Siglinda Perathoner1, Gabriele Centi1, Chiara Genovese1, Claudio Ampelli1 1 Department of Chemical, Biological, Pharmaceutical and Environmental Sciences (ChiBioFarAm) – University of Messina, ERIC aisbl and CASPE/INSTM, V.le F.Stagno d'Alcontres, 31 – 98166 Messina, Italy.
12:20 – 12:40	OR116	Jenny Grazia Vitillo – Department of Science and High Technology and INSTM, Università degli Studi dell'Insubria, Como (Italy) *Two In, One Out: Molecular Architectures for Efficient Photon Upconversion* Soumitra Manna1, Francesca S. Freyria2, Barbara Bonelli2, Jenny G. Vitillo,1 1 Department of Science and High Technology and INSTM, Università degli Studi dell'Insubria, Via Valleggio 9, I-22100 Como, Italy. 2 Department of Applied Science and Technology and INSTM-Unit of Torino Politecnico, Corso Duca degli Abruzzi 24, Politecnico di Torino,10129 Torino, Italy.
12:40 – 13:00	OR117	Łukasz Cichocki – Gdańsk University of Technology, Department of Sanitary Engineering, Gdańsk (Poland) *Catalytical degradation of haloacetic acids (HAA) in H_2/CO_2/Xe-UV system – Advanced Reduction Process (ARP) for wastewater treatment* Łukasz Cichocki, Grzegorz Boczkaj Gdańsk University of Technology, Department of Sanitary Engineering, St. Narutowicza 11/12, 80-233 Gdańsk, Poland.
13:00 – 15.00	Lunch Break	
15.00 – 15:20	OR125	Muhammad Sabir – University of Messina, ChiBioFarAm, Messina (Italy) *Novel APPJ-thermal hybrid system for methane decomposition* Francesco Pio Abramo1, Muhammed Sabir1, Palmarita Demoro1, Siglinda Perathoner, Gabriele Centi1, Ruben Bartali2, Alireza Ganjovi2, Salvatore Abate1 1University of Messina, Department of ChiBioFarAm (Industrial Chemistry), V.le F. Stagno d'Alcontres, Messina, Italy. 2 Fondazione Bruno Kessler, Via Sommarive 18, Trento, Italy.
		Short Orals
15:20 – 15:30	SO126	Kazuki Shun – Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, Osaka (Japan) *Hydrogen spillover on a non-reducible metal oxide comprising earth-abundant elements and its catalysis* Kazuki Shun1, Kohsuke Mori,1, Takumi Kidawara1, Hiromi Yamashita1 1 Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka Suita Osaka 565-0871, Japan

15:30 – 15:40	SO127	Hirohisa Tanaka – Kwansei Gakuin University, 1 Gakuen-Uegahara, Sanda, Hyogo 669-1330, Japan *STACY: International collaboration towards liquefied hydrogen safety* Hirohisa Tanaka, 1, Ernst Arndt Reinecke2, Nabiha Chaumeix3, Ahmed Bentaib4, Daiju Matsumura5, Masashi Taniguchi6, Shannon Krenz2, Tomohito Nakayama1, Shinya Uegaki1, Itsuki Jinjo1, Seita Kurono1 1 Kwansei Gakuin University, 1 Gakuen-Uegahara, Sanda, Hyogo 669-1330, Japan 2 Forschungszentrum Jülich GmbH (FZJ), 52425 Jülich, Germany 3 Centre National de la Recherche Scientifique (CNRS), Orléans, France. 4 Institut de Radioprotection et de Sûreté Nucléaire (IRSN), Fontenay-aux-Roses, France. 5 Japan Atomic Energy Agency, SPring-8, 1-1-1 Koto, Sayo, Hyogo 679-5148, Japan 6 Daihatsu Motor Co., Ltd., 21-1 Momozono, Ikeda, Osaka 563-8651 Japan
15:40 – 15:50	SO128	Piercosimo Vedele – POLITO, Turin (Italy) *Deactivation and kinetic models of catalytic methane pyrolysis over Fe/Al_2O_3 catalysts for a fluidized bed reactor integrated system* Piercosimo Vedele1, Enrico Sartoretti1, Fabio Salomone1, Massimiliano Antonini2, Samir Bensaid1 1Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129, Turin, Italy. 2 Hysytech srl, Via I Maggio 5, 10043, Orbassano, Italy.
15:50 – 16:00	SO129	Ramazan Yildirim – Boğaziçi University, Department of Chemical Engineering, Istanbul (Türkiye) *Machine learning analysis of halide perovskite for photocatalytic CO_2 reduction and water splitting* Beyza Yilmaz, Ramazan Yildirim Boğaziçi University, Department of Chemical Engineering, 34342, Istanbul, Türkiye.
16:00 – 16:10	SO130	Dorottya Szalay – Wolfson Catalysis Centre, Department of Chemistry, University of Oxford, Oxford, (UK) *Magnetic field-enhanced electrochemical oxygen evolution reaction using $Co_3O_4/BaFe_{12}O_{19}$ co-catalyst system* Dorottya Szalay1, Amy Radford1, Chen Wu2, Shik Chi Edman Tsang1 1 Wolfson Catalysis Centre, Department of Chemistry, University of Oxford, Oxford, OX1 3QR, United Kingdom 2 School of Materials Science and Engineering, State Key Laboratory of Silicon and Advanced Semiconductor Materials, Zhejiang University, Hangzhou 310027, China
16:10 – 16:20	SO131	Hajime Suzuki – Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto (Japan) *Spontaneous Adsorption of Iridium Chloride Complex on oxychloride photocatalysts Provides Efficient and Durable Reaction Site for Photocatalytic Water Oxidation* Hajime Suzuki,1 Kengo Minamimoto,1 Yusuke Ishii,1 Osamu Tomita,1 Akinobu Nakada,1 Shunsuke Nozawa,2 Ryu Abe,1 1Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan 2Photon Factory (PF), Institute of Materials Structure Science (IMSS), High Energy Accelerator Research Organization (KEK), Tsukuba, Ibaraki 305-0801, Japan
16:20 – 16:30	SO132	Saman Noroozi – Dept. of Applied Science and Technology, POLITO, Turin (Italy) *Evaluation of Cu- and CuZn-Exsolved Catalysts for the CO_2 Hydrogenation to MeOH* Eleonora Calì1, Saman Noroozi1, William Skinner2, David J. Payne2,3, Fabio Salomone1, Samir Bensaid1 1Dept. of Applied Science and Technology, Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129 Turin, Italy. 2 Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, U.K. 3 NEOM Education, Research, and Innovation Foundation, Al Khuraybah, Tabuk 49643-9136, Saudi Arabia
16:30 – 17:00	Coffee-Break	

17:00 – 17:20	OR118	Masaru Ogura – Institute of Industrial Science, The University of Tokyo, Komaba, Tokyo (Japan) *Transient and catalytic NO direct decomposition by irradiating microwave* Maya Chatterjee, Misaki Kimura, Masateru Nishioka, Masaru Ogura Institute of Industrial Science, The University of Tokyo, Komaba, Tokyo, Japan.
17:20 – 17:40	OR119	Kalle Weidauer – 1TU Bergakademie Freiberg, Institute of Energy Process Engineering and Chemical Engineering, Freiberg (Germany) *Removal of formaldehyde, carbon monoxide and methane from lean gas engine exhaust gases using precious metal-free catalysts* Kalle Weidauer1, Sven Kureti1 1TU Bergakademie Freiberg, Institute of Energy Process Engineering and Chemical Engineering, Fuchsmühlenweg 9D, 09599 Freiberg, Germany.
17:40 – 18:00	OR120	Margarita Popova – Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Sofia (Bulgaria) *CO_2 capture on the amino-modified mesoporous silica* Margarita Popova,1, Svilen Simeonov1, Ivailo Slavchev1, Yavor Mitrev1, Pavletta Shestakova1, Stela Grozdanopva1, Ivalina Trendaflova1 1 Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, acad. G. Bonchev str., bl. 9, Sofia, Bulgaria.
18:00 – 18:20	OR121	Edyta Tabor – J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Prague (Czech Republic) *Nature of Cu active centres in ferrierite based catalysts responsible for direct CO_2 transformation to platform chemicals* Julia Sobalska1,2, Kinga Mlekodaj3, Karolina Tarach1, Olena Tynkevych1, Dalibor Kaucký3, Jiri Dedecek3, Mark Newton3, Kinga Gòra-Marek1, and Edyta Tabor3 1Faculty of Chemistry, Jagiellonian University in Kraków, Gronostajowa 2, 30-387 Kraków, Poland. 2 Doctoral School of Exact and Natural Sciences, Jagiellonian University in Krakow, Łojasiewicza 11, 30-348 Krakow, Poland. 3 J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Dolejškova 2155/3, 182 23 Prague 8, Czech Republic.
18:20 – 18:40	OR122	Leonarda Francesca Liotta – CNR, ISMN, Palermo (Italy) *Ag/$Ce_{1-x}Mn_xO_2$ Catalysts for Soot Oxidation: Role of Ce/Mn Molar Ratio* Ekaterina S. L'vova,1 Tamara S. Kharlamova,1 Maria V. Grabchenko,1 Olga V. Vodyankina,1 Eleonora La Greca,2 and Leonarda F. Liotta2 1 Tomsk State University, 36 Lenin Ave., Tomsk, 634050, Russian Federation 2 CNR, ISMN, Via Ugo La Malfa 153, 90146-Palermo, Italy
		Short Orals
18:40 – 18:50	SO141	Stefania Volante – University of Pisa, Department of Chemistry and Industrial Chemistry, Pisa (Italy) *Sustainable energy storage materials from waste hazelnut shell biomass* Stefania Volante1, Domenico Licursi1, Federico Maria Vivaldi1, Pietro Zaccagnini2, Federico Bella2, Fabio Di Francesco1, Claudia Antonetti1 1University of Pisa, Dept Chem and Industrial Chemistry, Via G. Moruzzi 13, Pisa, Italy 2 Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129, Torino, Italy
18:50 – 19:00	SO142	Jennifer Cueto – Thermochemical Processes Unit, IMDEA Energy, Madrid (Spain) *Improving oil quality from waste plastics pyrolysis: aromatization and dehalogenation activity using MFI zeolites* Jennifer Cueto,1, Alberto Pinto1,2, Lidia Amodio1,2, Pavla Eliášová3, Patricia Pizarro1,2, Kenta Iyoki4, Tatsuya Okubo4, Tareq W.M. Amen5, Nao Tsunoji5, Jiří Čejka3, David P. Serrano1,2 1 Thermochemical Processes Unit, IMDEA Energy, Avda. Ramón de la Sagra 3, 28935, Móstoles, Madrid, Spain 2 Chemical and Environmental Engineering Group, Rey Juan Carlos University, Móstoles, Madrid, Spain

		3Dep. of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Prague, Czech Republic 4Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Tokyo, 113-8656, Japan 5Department of Applied Chemistry, Graduate School of Advanced Science and Engineering, Hiroshima University, 1-4-1 Kagamiyama, Hiroshima, 739-8527, Japan
19:00 – 19:10	SO143	Withdrawn
19:10 – 19:20	SO144	Alessandra Beretta – Dipartimento di Energia, POLIMI, Milano (Italy) *Kinetic Investigation of Ammonia Decomposition over Ru/CeO2 Catalysts Synthesized by Conventional IWI and Novel Mechanochemical Approaches* Yi Qiu1, Ivan Conti1, Nicole Bendazzoli1, Rudy Calligaro2, Alessandro Trovarelli2, Elisabetta Iengo3, Enzo Alessio3 and Alessandra Beretta1 1Dip Energia, Politecnico di Milano, Via Lambruschini 4, 20156, Milano, Italy 2 Dipartimento Politecnico di Ingegneria e Architettura, Università degli Studi di Udine, via del Cotonificio 108, 33100, Udine, Italy 3 Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste, Via L. Giorgieri 1, 34127, Trieste, Italy
19:20 – 19:30	Closing	

20:15 – 23:00	Banquet

P1 - POSTER SESSION 1 - 02/06/2025		
Nr.	Presenter	Title – Authors - Affiliations
P1-1	Asad Asadli	*Development of Catalyst Bed Concepts for Induction Heating for Emission Control* Asad ASADLI,1, Paolo DOLCET2, Vishrant KUMAR3, Alexis BORDET3, Silvia GROSS2, Moritz WOLF1,4 1Karlsruhe Institute of Technology, Institute of Catalysis Research and Technology, Hermann-von-Helmholtz-Platz 1, Eggenstein-Leopoldshafen, Germany. 2 University of Padova, Department of Chemical Sciences, Via Francesco Marzolo 1, Padova, Italy. 3 Max Planck Institute of Chemical Energy Conversion, Stiftstrasse 34-36, Mülheim an der Ruhr, Germany. 4 Karlsruhe Institute of Technology, Engler-Bunte-Institut, Engler-Bunte-Ring 7, Karlsruhe, Germany.
P1-2	Rizwan Asghar	*Optimizing Performance of Ce/Zr/Pr-based Gasoline Soot Oxidation Catalysts by Mechanochemical Synthesis* Rizwan Asghar1, Carla de Leitenburg1, Rudy Calligaro1, Alessandro Trovarelli1 1University of Udine, DPIA, Udine, Italy
P1-3	Dorsaf Bouazzi	*DFT Insights and Experimental Evaluation of MnCeOx/HAP Catalysts for Efficient Phenol Degradation in CWAO* D. Bouazzi1,2, A. Cajumi1,2, M. Samperi2, F. Randazzo2, G. Bonura2, C. Cannilla2, F. Arena1,2 1Dipartimento di Ingegneria, Università degli Studi di Messina, Viale F. Stagno D'Alcontres 31, I-98166 S. Agata (Messina), ITALY. 2 Istituto CNR-ITAE ''Nicola Giordano'', Via Salita S. Lucia 5, I-98126 S. Lucia (Messina), Italy.
P1-4	Rachele Braido	*Recyclable Ni@Al2O3 catalyst for Dry Reforming of Methane* Rachele Braido,1, Giulia Da Pian,1 Irene Martin,2 Giuseppe Cruciani,3 And Michela Signoretto1 1 Department of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice, and INSTM RUVe Via Torino 155, 30172-Venezia, Italia 2 Functional Nanosystems, Italian Institute of Technology (IIT), Via Morego 30, 16163 Genoa Italy, and Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 34, 10129 Turin Italy 3 Department of Physics and Earth Science, University of Ferrara, Via Saragat 1, 44122-Ferrara, Italia
P1-5	Nourrdine Chaouati	*withdrawn*
P1-6	Wei-Yu Chen	*Development of Multi-Emission Fluorescent Carbon Dot-Polyester Composites for Application as Tracers in Recycled Polyester Textile Fibers* Wei-Yu Chen Department of Materials Engineering, National Pingtung University of Science and Technology, Pingtung, Taiwan R.O.C
P1-7	Andrea De Giacinto	*Effect of catalyst composition on the activity and stability of Pt-Ni/ MgAlOx methane steam reforming catalysts* Andrea De Giacinto1, Enrico Tusini1, Dmitry Doronkin1,2, Maria Casapu1, Jan-Dierk Grunwaldt1,2, 1 Karlsruhe Institute of Technology, Institute for Chemical Technology and Polymer Chemistry, Engesserstraße 18-20, 76131 Karlsruhe, Germany 2 Karlsruhe Institute of Technology, Institute of Catalysis Research and Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
P1-8	Jacopo De Maron	*Asymmetric ketones intermediates by cross-ketonization* Jacopo De Maron, Gaetano Maria D'onofrio, Tommaso Tabanelli, Andrea Fasolini, Francesco Basile, Fabrizio Cavani University of Bologna, "Toso Montanari" Industrial Chemistry Dept., Viale Risorgimento 4, Bologna, Italy.

P1-9	Bezawit Z. Desalegn	*Tailoring Active Sites Towards High Selectivity for Paired-Electrochemical Biomass Upgrade over Medium/High-Entropy Sulfide Aerogels* Bezawit Z. Desalegn, and Jeong Gil Seo Hanyang University, Department of Chemical Engineering, 04763, Seoul, South Korea. Hanyang University, Clean-Energy Research Institute, 04763, Seoul, South Korea.
P1-10	Francesco Di Renzo	*Biodiesel improvement by skeletal isomerization on hierarchical zeolites* Jonathan Fabian Sierra-Cantor1, Olinda Gimello1, Luca Bernardi2,3, Anne Aubert-Pouëssel1, Carlos-Alberto Guerrero-Fajardo4, Francesco Di Renzo,1, Nathalie Tanchoux1, Corine Gérardin1 1 Université de Montpellier-CNRS-ENSCM, ICGM, Montpellier, France. 2 Alma Mater Studiorum Università di Bologna, Dip. Chimica Industriale "Toso Montanari", Bologna, Italy. 3 Alma Mater Studiorum Università di Bologna, C3 Center for Chemical Catalysis, Bologna, Italy. 4 Universidad Nacional de Colombia, Departamento de Quimica, Bogotá, Colombia.
P1-11	Jinpeng Du	*Towards rational design of Cu-SSZ-13 catalysts with less N_2O formation in NH_3-SCR reaction* Jinpeng Du1, Jianqi Liu2, Yulong Shan1, Wenpo Shan2, Yunbo Yu1, Hong He1, 2 1Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Haidian District, Beijing, 100085, China. 2Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China.
P1-12	Michele E. Fortunato *(replaces L. Lisi)*	*Promoted lanthanum oxysulfates as regenerable catalysts for soot oxidation in GPFs* Elisabetta M. Cepollaro1, Stefano Cimino1, Michele E. Fortunato1, Luciana Lisi,1 1Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili (STEMS) – CNR, P.le Tecchio 80 – 80125 Napoli, Italy.
P1-13	Nadia Grifasi	*Gold nanoparticles on manganese oxides with different crystalline structures: enhancing low-temperature air pollutants abatement* Nadia Grifasi1, Francesca Liuzzi2, Eleonora Cali'1, Samir Bensaid1, Nunzio Russo1, Fabio Deorsola1, Nikolaos Dimitratos2, Stefania Albonetti2, Fabrizio Cavani2, Debora Fino1, Marco Piumetti1 1Polytechnic of Turin, Department of Applied Science and Technology, Corso Duca Degli Abruzzi, 24, 10129, Turin, Italy 2 Alma Mater Studiorum - Bologna University, Department of Industrial Chemistry "Toso Montanari", Via P. Gobetti, 85, 40129, Bologna, Italy
P1-14	Victor Zaghini Francesconi	*withdrawn*
P1-15	Shota Hamada	*Oxygen Storage Materials in Automotive Catalysts: Composition of CZY* Shota Hamada1, Daiju Matsumura2, Shinya Uegaki1 , Hidetaka Tanabe1 , Tomohito Nakayama1, Itsuki Jinjo1, Seita Kurono1, Masami Nakamoto3, Tomohisa Mizuno4,Takashi Goto4, Hirohisa Tanaka1 1 Kwansei Gakuin University, Graduate School of Science and Technology, Sanda, Hyogo, Japan. 2 Japan Atomic Energy Agency, SPring-8., 1-1-1 Koto Sayo, Sayo, Hyogo, Japan. 3 Daihatsu Motor Co., Ltd., 2-1-1 Momozono, Ikeda, Osaka, Japan. 4 Cataler Corporation, 1905-10 Shimonobe, Iwata, Shizuoka, Japan.
P1-16	Olaf Hinrichsen *(replaces Anne Niederdränk)*	*Optimizing Iron-Containing Beta Zeolites: Influence of Synthesis Methods on Methane Oxidation Performance* Anne Niederdränk,1,2, Merle Blum1,2, Olaf Hinrichsen1,2 1 Technical University of Munich, School of Natural Sciences, Lichtenbergstr. 4, 85748 Garching, Germany. 2 Technical University of Munich, Catalysis Research Center, Ernst-Otto-Fischer-Str. 1, 85748 Garching, Germany.

P1-17	Younghwan Im	*NH3 decomposition of Al2O3 bead surface modified Ru catalysts to produce carbon-free hydrogen* 1Younghwan Im, 1Sung Min Kwon, 1Minsik Kim, 1Youngmin Kim, 1Ho-Jeong Chae, 1Hydrogen & C1 Gas Research Center, Korea Research Institute of Chemical Technology, 141 Gajeong-ro, Yuseong-gu, Daejeon, Republic of Korea.
P1-18	Aleksandra Jankowska	*Ti-MCM-22 catalysts for selective oxidation of organic sulphides by H_2O_2* Aleksandra Jankowska, Wiktoria Dubiel, Andrzej Kowalczyk, Małgorzata Rutkowska, Lucjan Chmielarz Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, 30-387 Kraków, Poland.
P1-19	Weijie Ji	*Defect-rich Mo/MoO_2 catalyst for efficient peroxymonosulfate activation and refractory pollutants degradation* Hongjun FANG, Hui GUO, Xinzhen FENG, Weijie JI Key Laboratory of Mesoscopic Chemistry, MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China
P1-20	Azusa Kamiyama	*Process Informatics of High-Entropy Alloy for Automotive Catalysis* Azusa Kamiyama1, Kohei Kusada2,3, Hiromasa Kaneko4, Megumi Mukoyoshi2, Masafumi Sakota1, Hiroto Tsuchiya1, Atsushi Furukawa1, Hiroshi Kitagawa2 and Hitoshi Mikami1 1Honda R&D Co., Ltd., Innovative Research Excellence, 4630 Shimotakanezawa, Haga-machi, Haga-gun, Tochigi, Japan. 2Kyoto University, Division of Chemistry, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto, Japan 3Kyoto University, The Hakubi Center for Advanced Research, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto, Japan 4Meiji University, Department of Applied Chemistry, 1-1-1 Higashi-Mita, Tama-ku, Kawasaki, Kanagawa, Japan
P1-21	Youngmin Kim	*withdrawn*
P1-22	Moon Hyeon Kim	*withdrawn*
P1-23	Min Sik Kim	*Complete oxidation of methane over Pd/zeolite catalysts for lowering the reaction temperature* Min Sik KIM1, Younghwan IM1, Youngmin KIM1, Yeon Jin LEE1, You-Jin LEE1, Ho-Jeong CHAE,1 1Korea research institute of chemical technology, Hydrogen & C1 gas research center, 141 Gajeong-ro Yuseong-gu, Daejeon, South Korea.
P1-24	Andrii Kostyniuk	*Sustainable conversion of biomass waste to levulinic acid and hydrochar via wet torrefaction with H-Beta zeolite catalyst* Andrii Kostyniuk1, Blaž Likozar1 1National Institute of Chemistry, Department of Catalysis and Chemical Reaction Engineering, Hajdrihova 19, Ljubljana, 1001, Slovenia
P1-25	Andrzej Kowalczyk	*Bimetallic LDHs origin catalysts containing Co, Fe and Ni for ammonia decomposition to hydrogen and nitrogen* Andrzej Kowalczyk, Lucjan Chmielarz Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, Kraków, Poland.
P1-26	Hwajun Lee	*withdrawn*
P1-27	Elena Mariani	*Impact of electroplating parameters on palladium hydride phases and hydrogen desorption dynamics* Elena Mariani1,2,3, Margherita Verrucchi1, Ambra Pelagatti1, Fabio Biffoli1, Walter Giurlani1,2, Pierandrea Lo Nostro1, Marco Pagliai1, Massimo Innocenti1,2 1 Department of Chemistry, UNIFI, via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy.

		2 INSTM, via Giuseppe Giusti, 9, 50121, Florence (FI), Italy. 3 Eco-Tech Finish s.r.l., Z.I. San Zeno, Strada C 27, 52100 Arezzo, AR, Italy.
P1-28	Francesco Montanari	*Electrodeposition of nanostructured metals on silicon. A focus on the rhodium/n-doped silicon composite as a promising platform for energy applications* Francesco Montanari1, Giulio Pappaianni1, Francesco Visconti1, Patrick Nunziati1, Walter Giurlani1,2, Massimo Innocenti1,2 1University of Florence, Department of Chemistry "Ugo Schiff", via della Lastruccia 3-13, Sesto Fiorentino 50019, Italy. 2 National Interuniversity Consortium of Material Science and Technology (INSTM), 50121, Italy.
P1-29	Nelly Morrone	*From sewage scum up to lipids production using oleaginous yeasts as biocatalysts* Nelly Morrone1, Nicola Di Fidio1, Valeria D'ambrosio2, Claudia Antonetti1, Anna Maria Raspolli Galletti1, Carlo Pastore2 1 Department of Chemistry and Industrial Chemistry, University of Pisa, Via G. Moruzzi 13, 56124 Pisa, Italy 2 Water Research Institute (IRSA), National Research Council (CNR), Viale De Blasio 5, 70132 Bari, Italy
P1-30	Akira Oda	*Durable Ethane Oxidation to Ethanol: Insights into SMSI Effects on TiO2-Supported Pt Catalysts* Akira Oda,1, Terufusa Inagaki1, Koyo Ichino1, Yuta Yamamoto2, Yuya Kimura1, Kyoichi Sawabe1, Atsushi Satsuma1 1 Department of Materials Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan. 2 Institute of Materials and Systems for Sustainability, Nagoya University, Nagoya 464-8603, Japan.
P1-31	Takeshi Ohtsu	*Promotion Effect of Water Vapor on co-Adsorption of NO on Pd/Zeolite* Takeshi OHTSU1, Nao TSUNOJI2, Akira ODA1, Atsushi SATSUMA1 1Nagoya University, Department of Materials Chemistry, Furo-cho, Chikusa-ku, Nagoya, Japan. 2 Hiroshima University, Department of Applied Chemistry, Kagamiyama 1-4-1, Higashi-hiroshima, Japan.
P1-32	Piotr Pietrzyk	*Decomposition of model organic pollutants via wet peroxidation – the activity of composite copper catalysts in the generation of ROS* Wiktor Czerwonka, Kamila Sobańska, Piotr Pietrzyk Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, 30-387 Krakow, Poland.
P1-33	Anna Maria Raspolli Galletti	*Esterification of hexanoic acid to hexyl hexanoate with heterogeneous acid catalysts: preliminary evaluations with Amberlyst and niobium- zirconium-phosphates* Anna Maria Raspolli Galletti, Leonardo Carmassi, Nicola Di Fidio, Sara Fulignati, Claudia Antonetti, Domenico Licursi University of Pisa, Department of Chemistry & Industrial Chemistry, Via Giuseppe Moruzzi, 13, Pisa, Italy.
P1-34	Vincenzo Russo	*Ibuprofen photodegradation under visible light promoted by Fe-doped nano CeO2* Vincenzo Russo,1, Rosanna Paparo1, Olimpia Tammaro2, Martino Di Serio1, Serena Esposito2 1 Università di Napoli 'Federico II', Department of Chemical Sciences, Napoli, Italy. 2 Department of Applied Science and Technology and INSTM Unit of Torino – Politecnico, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy.
P1-35	Atsushi Satsuma	*Mechanistic Study on Generation and Growth of Ash Particles from Lubricant Additives* Junya Onoda, Akira Oda, Atsushi Satsuma Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan.
P1-36	Elena Spennati	*(Ni,Cu) catalysts for ethanol dehydrogenation: performances vs. synthesis* Elena Spennati1,2, Giovanni Pampararo3, Gabriella Garbarino1,2, Paola Riani2,3 1 University of Genova, Dicca Dept., Genova, 16145 (Italy) 2 INSTM, Udr Genova, 16146 (Italy)

		3 University of Genova, DCCI Dept., Genova, 16146 (Italy)
P1-37	Dorottya Szalay	*Rare earth element modified nickel phosphide nanoparticles as electro- and photocatalysts for hydrogen generation reactions* Dorottya Szalay1, Shik Chi Edman Tsang1 1 Wolfson Catalysis Centre, Department of Chemistry, University of Oxford, Oxford, OX1 3QR, United Kingdom
P1-38	Hidetaka Tanabe	*In-situ XAFS Analysis on Redox Dynamics of Precious Metal-supported Ce Complex Oxides* Hidetaka Tanabe1, Daiju Matsumura3, Shinya Uegaki2, Shota Hamada2, Takehisa Oseki4, Tomohisa Mizuno4, Shunsuke Oishi4, Masami Nakamoto5, Tetsurou Oonishi5, Kazuya Yasuda5, Hirohisa Tanaka2, 1Kwansei Gakuin University, Program of Materials Science, Sanda, Hyogo Japan. 2Kwansei Gakuin University, Graduate School of Science and Technology, Sanda, Hyogo Japan. 3 Japan Atomic Energy Agency, SPring-8, 1-1-1 Koto Sayo, Sayo, Hyogo, Japan. 4Cataler Corporation, 1905-10 Shimonobe, Iwata, Shizuoka, Japan. 5Daihatsu Motor Co., Ltd., 2-1-1 Momozono, Ikeda, Osaka, Japan.
P1-39	Maria Luisa Testa	*MW-assisted Pt@CsN_4/TiO_2 composites for glycerol photoreforming for H2 production* M.C. Herrera-Beurnio, C. Aliotta2, F.J. López-Tenllado1, M. Russo2, F. J. Urbano 1, A. Marinas1, M. L. Testa2 ' Departamento de Química Orgánica, Instituto Químico para la Energia y el Medioambiente (IQUEMA), Universidad de Córdoba, E-14071 Córdoba, Spain 2 Istituto per lo Studio dei Materiali Nanostrutturati, Consiglio Nazionale delle Ricerche (ISMN-CNR), Via Ugo La Malfa 153, 1-90146, Palermo, Italy
P1-40	Margarita Popova	*CO_2 methanation on the Ni-Mn-modified mesoporous silica* Margarita Popova,1,2, Grigoria Teohari 1, Gloria Issa1, Daniela Kovacheva3, Martin Kormunda4 1 Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, acad. G. Bonchev str., bl. 9, Sofia, Bulgaria 2 National Centre of Excellence Mechatronics and Clean Technologies, Bulgaria 3 Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, acad. G. Bonchev str., bl. 11, Sofia, Bulgaria 4 Faculty of Science, University of Jan Evangelista Purkyně, Pasteurova 3632/15, 400 96 Ústí nad Labem, Czech Republic

P2 - POSTER SESSION 2 – 03/06/2025		
Nr.	Presenter	Title – Authors - Affiliations
P2-1	Andrzej Adamski	*Oxide and zeolitic systems of catalytic importance synthesized from fly ashes from industrial energy sector* Paweł RYBOWICZ1, Rafał PANEK2, Artur ŁAGOSZ3, Barbara GIL1, Wiesław ROTH1, Wojciech FRANUS2, Andrzej ADAMSKI,1 1Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, 30-687 Kraków, Poland. 2Lublin University of Technology, Faculty of Civil Engineering and Architecture, Nadbystrzycka 40, 20-618 Lublin, Poland. 3AGH - University of Science and Technology, Faculty of Material Science and Ceramics, Mickiewicza Ave. 30, 30-059 Kraków, Poland.
P2-2	Stefania Albonetti	*Simultaneous waste remediation and carbon capture via CO_2 mineralization over industrial basic wastes* Alessandro Allegri1, Valentina Scognamiglio2, Maria Chiara Bignozzi2,3, Alessandro Dal Pozzo3, Alberto Renato De Angelis4, Roberto Millini4, Stefania Albonetti,1 1 University of Bologna, Department of Industrial Chemistry "Toso Montanari", C3 – Center for Chemical Catalysis, CIRI-FRAME, Via P. Gobetti 85, Bologna, Italy. 2 Centro Ceramico, Via Valle d'Aosta, 1, Sassuolo, MO, Italy 3 University of Bologna, Department of Civil, Chemical,– DICAM, via U. Terracini 28, Bologna, Italy. 4 ENI S.p.A. Research and Technological Innovation Department, Via F. Maritano 26, San Donato Milanese, Italy
P2-3	Sukomol Barua	*3D NiMnCo trimetallic electrocatalysts with cauliflower curd-shaped micro-sized nodular morphology for an efficient and sustainable hydrogen evolution reaction in alkaline media and simulated seawater* Sukomol Barua, Aldona Balčiūnaitė, Jūrate Vaičiūnienė, Loreta Tamašauskaitė-Tamašiūnaitė and Eugenijus Norkus Center for Physical Sciences and Technology (FTMC), Department of Catalysis, Saulėtekio ave. 3, LT-10257, Vilnius, Lithuania
P2-4	Nassima Berroug	*Effect of Ni particle size on the efficiency of Ni/HAP catalysts in the decarbonization processes* Nassima Berroug, Miguel A. Gutiérrez-Ortiz, Juan R. González-Velasco, Zouhair Boukha Chemical Technologies for Environmental Sustainability Group, Department of Chemical Engineering, Faculty of Science and Technology, University of the Basque Country UPV/EHU, P.O. Box 644, E-48080, Bilbao, Spain
P2-5	Michele Bigica *(replaces Antonella Gervasini)*	*Circular Economy-Driven Synthesis of Hydroxyapatites from Ash: A Comprehensive Analysis of Surface and Bulk Properties* Antonella Gervasini,1 Sebastiano Campisi,1 Michele Bigica,1 Marta Tavoni,2 Simone Sprio,2 Anna Tampieri,2 Gina Postole3 1 Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 2013 Milano, Italy 2 Institute of Science, Technology and Sustainability for Ceramics, CNR, Via Granarolo 64, Faenza, Italy 3 Université Claude Bernard Lyon 1, CNRS, IRCELYON, F-69626 Villeurbanne, France
P2-6	Lidia Castoldi	*Preparation of Si-rich LTA zeolite for membrane reactors in e-methanol synthesis* Lidia Castoldi1, Luca Lietti1, Carlo Visconti1, Nadia Cerone2, Francesco Zimbardi2 1Politecnico di Milano, Department of Energy, LCCP group, via La Masa 34, 20156 Milano, Italy.

		2 ENEA, Energy Technologies and Renewable Sources Department, ss 106, 75026 Rotondella, Italy.
P2-7	Jiyoung Chae	*Synthesis of sustainable polyol by simultaneous utilization of CO2 and waste PET* Jiyoung Chae, Yein Kim, Joon Hyun Baik Department of Chemical and Biological Engineering, Sookmyung Women's University, 04310, Seoul, Republic of Korea
P2-8	Hsin-Yu Chen	*Understanding Methanation Inhibition Using Cs-promoted Defective Carbon Supports for Ru Catalysts in Ammonia Production* Cheng-Hsi Yeh1, Hsin-Yu Chen1,2, Shih-Yuan Chen3, Hsin-Yi Tiffany Chen,1,2,4 1 National Tsing Hua University, Department of Engineering and System Science, Hsinchu 300044, Taiwan. 2 National Tsing Hua University, Department of Materials Science and Engineering, Hsinchu 300044, Taiwan. 3 National Institute of Advanced Industrial Science and Technology (AIST), Energy Catalyst Technology Group, Energy Process Research Institute (EPRI), 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan. 4 National Tsing Hua University, College of Semiconductor Research, Hsinchu 300044, Taiwan.
P2-9	Imen Cherif	*Photocatalytic CO_2 reduction over TiO_2NT/g-C_3N_4 based heterostructures* Imen Cherif, Georgia Papanikolaou, Paola Lanzafame, Siglinda Perathoner, Gabriele Centi, Rosalba Passalacqua University of Messina, Department of Chemical, Biological, Pharmaceutical and Environmental Sciences (ChiBioFarAm) & INSTM CASPE (Lab. of Catalysis for Sustainable Production & Energy), Viale F. Stagno d'Alcontres 31, 98166 Messina, Italy
P2-10	Renaud Cousin *(replaces Eric Genty)*	*Influence of preparation method of CuAl mixed oxide issued from LDH for LDH for catalytic total oxidation of VOC -CO* Eric GENTY, Pierre Edouard DANJOU, Christophe POUPIN, Stéphane SIFFERT, Renaud COUSIN Université du Littoral Côte d'Opale, Unité de Chimie environnementale et Interactions sur le Vivant (UCEIV), 145 avenue Maurice Schumann, 59140 Dunkerque, France.
P2-11	Petar Djinović *(replaces Miha Okorn)*	*Utilization of visible light in the Reverse Water Gas Shift reaction over $Cu/Ce_x(Ti_{1-x})O_2$ catalyst* Miha Okorn1,2, Kristijan Lorber1 and Petar Djinović1,2 1National Institute of Chemistry, Hajdrihova 19, Ljubljana, Slovenia. 2 University of Nova Gorica, Vipavska 13, Nova Gorica, Slovenia.
P2-12	Elisabetta Finocchio	*SILCO Project: Waste-derived SILica-based porous solids for Carbon diOxide capture, storage and re-use catalytic technology* Lidia Castoldi1, Cinzia Cristiani,2, Barbara Di Credico3, Matteo Di Virgilio2, Elisabetta Finocchio,4, Luca Lietti1, Sergio Molina-Ramírez2, Roberto Scotti3, Lorenzo Vigano'3 1Dipartimento di Energia (Laboratory of Catalysis and Catalytic Processes), Politecnico di Milano (POLIMI), Via la Masa 34, Milano, Italy. 2Dipartimento di Chimica, Materiali e Ingegneria Chimica Giulio Natta, Politecnico di Milano (POLIMI), Piazza Leonardo Da Vinci 32, Milano, Italy. 3Dipartimento di Scienza dei Materiali, Università Milano-Bicocca (UNIMIB), Piazza dell'Ateneo Nuovo, 1, Milano, Italy. 4Dipartimento di Ingegneria Civile, Chimica e Ambientale, Università di Genova (UNIGE), Via all'Opera Pia 15, Genova, Italy.
P2-13	Francesca S. Freyria	*TiO_2/QDs nanocomposites for sustainable reactions: synthesis and characterization* Francesca S. Freyria1, Najeebullah Channa1, Francesco Pellegrino2, Jenny G. Vitillo,3 Nicoletta Di Taranto4, Michele Bucchieri1,5, Nicola Blangetti1, Barbara Bonelli1 11Department of Applied Science and Technology and INSTM-Unit of Torino Politecnico, Corso Duca degli Abruzzi 24, Politecnico di Torino,10129 Torino, Italy

		2 Department of Chemistry, University of Torino, via Giuria 5, 10125 Torino, Italy 3 Department of Science and High Technology and INSTM, Università degli Studi dell'Insubria, Via Valleggio 9, I-22100 Como, Italy 4Department of Chemistry, Università degli Studi di Bari Aldo Moro, 70125 Bari, Italy 5Departement of Chemistry, Biology and Biotechnologies- Università degli Studi di Perugia
P2-14	Suk Bong Hong	withdrawn
P2-15	Plaifa Hongmanorom	*The role of vanadium in silica-supported Ru catalysts for enhanced CO2 methanation* Plaifa HONGMANOROM1, Damien P. DEBECKER,1 1Institute of Condensed Matter and Nanoscience, UCLouvain, Place Louis Pasteur 1, Louvain-La-Neuve, Belgium.
P2-16	Peijun Hu	withdrawn
P2-17	Chiara Ingrosso	*Novel Hybrid Nanocomposites based on Au Nanoparticles Decorated Soot Carbon Nanoparticles for Electroanalytical Sensors* C. Ingrosso1,, F. Migliorini2, W. Aidli3, S. Dicorato4, P. S. Sfragano5, F. Spatafora5, G. V. Bianco4, V. Pifferi3, M. Striccoli1, M. Longhi3, G. Cappelletti3, M. L. Curri1,6, I. Palchetti5, L. Falciola3 1CNR-IPCF S.S. Bari, c/o Dept. of Chemistry, Università degli Studi di Bari, via Orabona 4, 70126 Bari, Italy 2CNR-ICMATE S.S. Milano, Via Cozzi 53, 20125 Milano, Italy 3Dept. of Chemistry, Università degli Studi di Milano, via Golgi 19, 20133 Milano, Italy 4CNR-NANOTEC Sez. Bari, c/o Dept. of Chemistry, Università degli Studi di Bari, Via Orabona 4, 70126 Bari, Italy 5Dept. of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy 6Dept. of Chemistry, Università degli Studi di Bari, Via Orabona 4, 70126 Bari, Italy
P2-18	Ren Itagaki	*Biphasic Z-Scheme Photocatalytic System Using a Phase-Migrating Electron Mediator* Ren ITAGAKI1,2, Akinobu Nakada1, Hajime Suzuki1, Osamu Tomita1, Ryu Abe1 1Kyoto University, Grad. Sch. of Eng., Kyoto daigaku-katsura, Nishikyo-ku, Kyoto, Japan. 2JSPS Research Fellow DC1, Kojimachi Business Center Building, 5-3-1 Kojimachi, Chiyoda-ku, Tokyo, Japan.
P2-19	Dobrina Ivanova	*Tribocatalytic Degradation of Chloramphenicol Using Eu-Doped ZnO Catalysts: A Sustainable Approach to Pharmaceutical Pollutant Removal* Dobrina IVANOVA1, Bozhidar STEFANOV2, Hristo KOLEV3, Nina KANEVA1 1Laboratory of Nanoparticle Science and Technology, Department of General and Inorganic Chemistry, Faculty of Chemistry and Pharmacy, University of Sofia, 1164 Sofia, Bulgaria 2Department of Chemistry, Faculty of Electronic Engineering and Technologies, Technical University of Sofia, 8 Kliment Ohridski Blvd, 1756 Sofia, Bulgaria 3Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., bl. 11, 1113 Sofia, Bulgaria
P2-20	Kenshin Chishima	*Efficient search for acetic acid synthesis pathway based on the bond disconnection process on Rh surface and Rh/metal oxide interface* Kenshin CHISHIMA1, Takumi MASUDA1, Hiroshi SAMPEI1, Koki SAEGUSA1, Sakuya HATTORI1, and Yasushi SEKINE1 1 Waseda University, Department of Applied Chemistry, 3-4-1, Okubo, Shinjuku-ku, Tokyo, Japan.

P2-21	Alexander Klyushin	*withdrawn*
P2-22	Koki Saegusa	*Theoretical Design of CeO_2-Based Materials for Enhanced RWGS-CL Performance* Koki SAEGUSA1, Takuma HIGO1, Shuhei ISHIZAKI1, Sota KAKIHARA1, Hiroshi SAMPEI1, and Yasushi SEKINE,1 1 Department of Applied Chemistry, Waseda University, 3-4-1, Okubo, Shinjuku, Tokyo, Japan.
P2-23	Athanasia Kotsaridou	*CO_2 hydrogenation to light olefins over fe-based mixed oxides derived from layered double hydroxides* Athanasia KOTSARIDOU1,, Antigoni MARGELLOU1, Evridiki MANDELA2, Michail KONSOLAKIS3, Georgios MARNELLOS4, Konstantinos TRIANTAFYLLIDIS1 1Aristotle University of Thessaloniki, Department of Chemistry, Thessaloniki, Greece 2University of Western Macedonia, Department of Mechanical Engineering, Kozani, Greece 3Technical University of Crete, School of Production Engineering and Management, Chania, Greece 4Aristotle University of Thessaloniki, Department of Chemical Engineering, Thessaloniki, Greece
P2-24	Hyeon-Bin Lee	*High-Throughput Optimization of Mo-Doped $BiVO_4$ Thin Films Using SPECM for Enhanced Photoelectrochemical Performance* Hyeon-Bin Lee1,2, Jae-Cheol Park1, Soe-Jin Jeong1, Si-Yun Jeong1, Jun-Seok Ha2, Tae-Won Kim,1 1 Energy & Nano Technology Group, Korea Institute of Industrials Technology 6, Cheomdan-gwagiro 208-gil, Buk-ku, Gwangju, 61012, Republic of Korea. 2 Department of Chemical Engineering, Chonnam National University 77, Yongbong, Buk-gu, Gwangju 500-757, Republic of Korea.
P2-25	Renzo A. Leeflang	*Core-Shell Chabazite Catalysts for the Tandem Catalysis of CO_2 to Light Hydrocarbons:* Renzo A. Leeflang1, Volkan Degirmenci2, Edman S.C. Tsang1, 1Wolfson Catalysis Centre, Department of Chemistry, University of Oxford, Oxford OX1 3QR, United Kingdom 2 School of Engineering, University of Warwick, Coventry, CV4 7AL, United Kingdom.
P2-26	Angeliki Lemonidou	*Selective catalytic cracking of plastic waste for naphtha-like pyrolysis oil production* Petros Soldatos1, Angeliki Lemonidou2, Konstantinos Triantafyllidis1, 1Aristotle University of Thessaloniki, Department of Chemistry, Thessaloniki, Greece. 2Aristotle University of Thessaloniki, Department of Chemical Engineering, Thessaloniki, Greece.
P2-27	Luca Lietti *(replaces Alessandro Porta)*	*Green NH_3 production from NOx stationary emissions* Giuseppe Nava1, Alessandro Porta1, Roberto Matarrese1, Luca Lietti1 1Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano – Via La Masa 34, 20156 Milan, Italy
P2-28	Marina Maddaloni	*Ionic Liquid-Assisted Synthesis of Fe-Ru Bimetallic Catalysts for Enhanced CO_2 Conversion to Lower Olefins with High Selectivity* Marina MADDALONI1, Ander CENTENO-PEDRAZO2, Simone AVANZI1, Nayan Jyoti MAZUMDAR2, Haresh MANYAR2 and Nancy ARTIOLI1 1CEEP Laboratory, Department of Civil Engineering, Architecture, Territory, Environment and Mathematics, University of Brescia, via Branze 38, 25123 Brescia, Italy; 2School of Chemistry and Chemical Engineering, Queen's University Belfast, David-Keir Building, Stranmillis Road, Belfast, BT9 5AG, UK

P2-29	Marina Maddaloni *(replaces Nancy Artioli)*	*Solid Catalyst with Ionic Liquid Layer (SCILL) for Direct CO_2 Hydrogenation to Methanol:Enhancing Performance and Stability* Giuseppe BAGNATO1, Emilia MORROW1, Hannah AGNEW1, Małgorzata SWADŹBA-KWAŚNY1 And Nancy ARTIOLI2 1School of Chemistry and Chemical Engineering, Queen's University Belfast, David-Keir Building, Stranmillis Road, Belfast, BT9 5AG, UK 2CEEP Laboratory, Department of Civil Engineering, Architecture, Territory, Environment and Mathematics, University of Brescia, via Branze 38, 25123 Brescia, Italy;
P2-30	Marco Pietro Mezzapesa	*Cu-Ce binary oxide catalysts for CO_2 hydrogenation to methanol: Operando FT-IR spectroscopy and kinetic study* Marco Pietro Mezzapesa, Fabio Salomone, Enrico Sartoretti, Raffale Pirone, Samir Bensaid Politecnico di Torino, Department of Applied Science and Technology (DISAT), Corso Duca degli Abruzzi 24, 10129 Turin, Italy.
P2-31	Sergio Molina-Ramírez	*Silica supported DFM catalysts for CO2 Capture, Storage and Re-use Technology. Comparative study with Al2O3-based model catalyst.* Sergio Molina-Ramírez1, Giuseppe Nava2, Cinzia Cristiani1, Barbara Di Credico3, Roberto Scotti3, Luca Lietti2, Lidia Castoldi2, Elisabetta Finocchio,4 1 Dipartimento di Chimica, Materiali e Ingegneria Chimica Giulio Natta, Politecnico di Milano, Milano, Italy. 2 Dipartimento di Energia (Laboratory of Catalysis and Catalytic Processes), Politecnico di Milano, Milano, Italy. 3 Dipartimento di Scienza dei Materiali, Università Milano-Bicocca, Milano, Italy. 4Dipartimento di Ingegneria Civile, Chimica e Ambientale, Università di Genova, Genova, Italy.
P2-32	Hadis Mortazavi Milani	*withdrawn*
P2-33	Fabian Neumann	*Getting CuO/ZnO/ZrO_2 in shape: Tableting of methanol catalysts* Fabian NEUMANN1, Lucas WARMUTH1, Thomas N. OTTO1, Thomas A. ZEVACO1, Michael ZIMMERMANN1, Stephan PITTER1, Moritz WOLF,1 1Karlsruhe Institute of Technology (KIT), Institute of Catalysis Research and Technology (IKFT), Hermann-von-Helmoltz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.
P2-34	Mauro Bracconi *(replaces Kaustav Niyogi)*	*Assessing the effect of catalyst structure on the competitive CO_2 hydrogenation pathways to CO and Methanol on Copper* Kaustav NIYOGI, Matteo MAESTRI Politecnico di Milano Laboratory of Catalysis and Catalytic Processes, Department of Energy Via La Masa 34, Milano 20156, Italy
P2-35	Nicola Panza	*Ni-doped tungsten carbide catalysts for the selective production of ethylene glycol from cellulosic materials* Nicola PANZA, Marta STUCCHI, Laura PRATI Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19 Milano Italy
P2-36	Amy Radford	*Structure-Activity Evolution of $AgNbO_3$ via Exsolution* Amy Radford1, Nathan Coltart1, Yiyang Li1, Edman Tsang1 1Wolfson Catalysis Centre, University of Oxford, Oxford, England
P2-37	Clara Saetta	*TiN based Single-Atom Catalyst in Aqueous Environment: a Step Towards the Experimental Complexity* Clara SAETTA1, Giovanni DI LIBERTO2, Gianfranco PACCHIONI3 1,2,3Università degli Studi Milano-Bicocca, Department. of Materials Science, Via Roberto Cozzi 55, Milan, Italy.

P2-38	Shokat Sarmad	*withdrawn*
P2-39	Stephane Siffert *(replaces Anthony Abou Rahhal)*	*CO_2 Purification of Industrial Flue Gas: The Role of Copper and Carbonate Species in the Selective Catalytic Reduction Process.* Abou Rahhal A.1, Genty E.1, Cousin R.1, Ponchel A.2, Noel S.2, Poupin C.1, Siffert S.1 1Univ. Littoral Côte d'Opale, UR 4492, UCEIV, Unité de Chimie Environnementale et Interactions sur le Vivant, F-59140, Dunkerque, France 2Univ. Artois, CNRS, Centrale Lille, Univ. Lille, UMR 8181, Unité de Catalyse et de Chimie du Solide (UCCS), rue Jean Souvraz, SP 18, 62300 Lens, France
P2-40	Giuseppe Sportelli	*withdrawn*
P2-41	Francesco Taddeo	*Sustainable synthesis of ketals from ethyl levulinate and glycerol* Francesco Taddeo, Rosa Vitiello, Rosa Turco, Riccardo Tesser, Vincenzo Russo, Martino Di Serio University of Naples Federico II, Chemical Sciences Department, Via Cintia, Napoli, Italy.
P2-42	Gitana Valeckytė	*Synthesis and Characterization of Nickel Cobalt Catalysts* Gitana Valeckytė, Zita Sukackienė, Jūratė Vaičiūnienė, Loreta Tamašauskaitė-Tamašiūnaitė, Eugenijus Norkus Department of Catalysis, Center for Physical Sciences and Technology (FTMC), Saulėtekio al. 3, LT-10257 Vilnius, Lithuania
P2-43	Elyes Bel Hadj Jrad *(replaces Michele Zanoni)*	*Nanofiber-reinforced composite Proton-Exchange Membranes* Michele Zanoni1, Elyes Bel Hadj Jrad,1,2, Elisabetta Petri1,2, Francesca Soavi1,2, Chiara Gualandi1 1Dept. of Chemistry "Giacomo Ciamician", University of Bologna, Via Selmi 2, 40126, Bologna, Italy 2Centre for the Environment, Energy, and Sea - Interdepartmental Centre for Industrial Research in Renewable Resources, Environment, Sea and Energy (CIRI-FRAME), University of Bologna, Viale Ciro Menotti 48, 48122, Marina di Ravenna, Italy

PLENARY and KEYNOTE ABSTRACTS



Design of Nanostructured Catalysts for Sustainable Energy and Environmental Uses

Hiromi YAMASHITA[1*]

[1]*Graduate School of Engineering, The University of Osaka, Suita, Osaka 565-0871, Japan*
** yamashita@mat.eng.osaka-u.ac.jp*

Significance and Relevance

The precise structural control of special reaction fields, such as the nanopores of zeolites, mesoporous silica, MOFs, and thin film interfaces, was achieved. This led to the successful precise design of single-site photocatalysts (isolated metal ions, photo-functional metal complexes), ultra-fine particle semiconductor photocatalysts, plasmonic catalysts, high-entropy alloy particle catalysts, and porous metal catalysts with unique structures distinct from conventional ones. These nano-designed high-activity catalysts were extended to environment-friendly reactions such as hydrogen cycling reactions (hydrogen production from water and hydrogen carrier molecules, hydrogen peroxide synthesis), carbon dioxide reduction reactions (synthesis of CO, formic acid, methanol, methane), and air-water purification, revolutionizing catalyst development.

Introduction and Motivations

Designs of “active sites", "reaction fields" and “energy injection” are important for catalyst development. In the nanospace of zeolite, mesoporous silica and MOF, it is possible to control the structure of catalytic active sites in forms of fine particles, clusters, molecules, and atomic moieties, and also possible to control the reaction fields with unique properties such as hydrophobicity and electrostatic fields. Ultrafine semiconductor photocatalysts, single-site photo-catalysts, plasmonic catalysts, nano-alloy catalysts, Yolk-shell catalysts, and MOF photocatalysts, can be designed for H_2 production, CO_2 fixation, H_2O_2 synthesis, and various selective reactions.

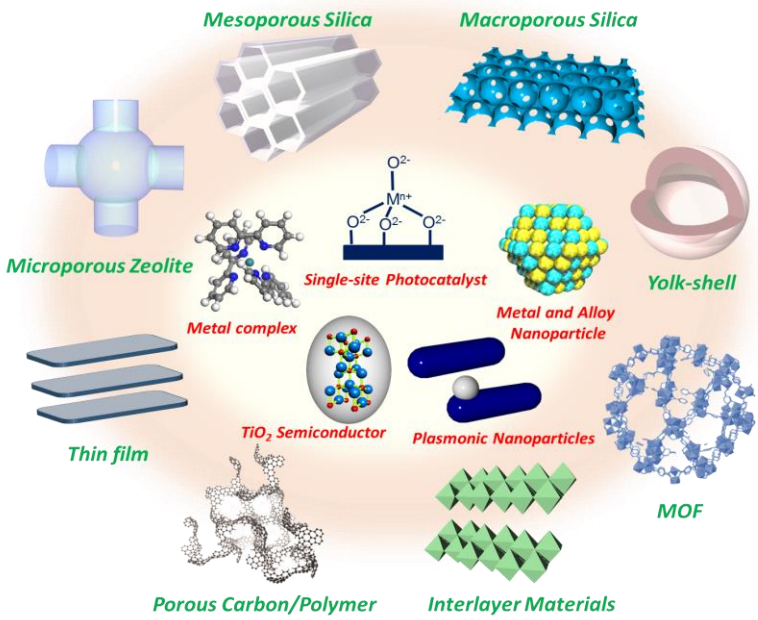


Figure 1 Design of mesostructured catalysts and photocatalysts using porous materials.

Results and Discussion

Design of Single-Site/Ultra-Fine Particle Photocatalysts in Nanospaces:

The focus was made on the ability of nanoporous materials such as zeolites to fuse metal ions in an isolated state, leading to the development of "single-site photocatalysts" with structures and properties significantly different from conventional photocatalysts by introducing metal ions into

pores and frameworks. Applications to CO_2 reduction and NO_X decomposition were attempted, clarifying the importance of surface coordination unsaturated sites (tetra-coordinated titanium oxide, bi-coordinate copper ions, etc.). Furthermore, high functionality was achieved by fixing photo-functional metal complexes as single-site photocatalysts in nanospaces, applied to hydrogen production from water. On the other hand, the hybrid of ultra-fine semiconductor particles and nanoporous materials was conducted, modifying pore surfaces (with hydrocarbon, fluorine, apatite, graphene, etc.) and improving spatial characteristics (hydrophilicity/hydrophobicity, electrostatic field, spatial volume) to achieve reactant concentration and reaction efficiency. Unique higher-order nanostructures such as macro/mesoporous structures, core-shell structures, and yolk-shell (hollow space) structures were developed, leading to further activity improvements. Particularly, high-efficiency CO_2 reduction was enabled by integrating basic polymers capable of concentrating CO_2 with CO_2 reduction catalysts in hollow spaces.

Design of Plasmonic/MOF Photocatalysts Utilizing Nanostructures:

Based on single-site photocatalysts, well-defined metal nanocatalysts were prepared and utilized for H_2O_2 synthesis and VOC combustion. Furthermore, by using rapid uniform heating via microwave heating and the regulated spaces of mesoporous materials, metal nanoparticles (Ag, PdAu, etc.) with precisely controlled shape, size, and color were prepared, leading to the development of plasmonic catalysts that can exhibit localized surface plasmon resonance under visible light irradiation and significantly enhance catalytic performance. Additionally, the design of metal-organic framework (MOF) photocatalysts aimed at H_2O_2 generation was conducted, creating reaction fields that inhibit the decomposition of generated H_2O_2 by hydrophobizing MOF surfaces. Furthermore, a two phases reaction system of water-organic solutions was developed, enabling the high-concentration production of H_2O_2.

Design of New Catalytic Materials Utilizing Hydrogen Spillover Phenomena:

A catalyst preparation method has been developed utilizing the "hydrogen spillover phenomena," in which hydrogen molecules diffuse as atomic hydrogen on the surface of oxides through metals. Whether hydrogen diffuses on the surface of the support or is doped into the support depends on the basicity, surface functional groups, oxygen defects, and crystal phase of the oxide support. On Mo oxide, hydrogen activated by Pt spills over and is doped into the Mo oxide in large quantities, resulting in the preparation of reduced H_XMoO_{3-y} with numerous oxygen defects, demonstrating high activity for CO_2 reduction by functioning as a photothermal conversion catalyst under visible light irradiation. On the other hand, on oxides such as CeO_2, active hydrogen diffuses on the surface through hydrogen spillover, allowing the low-temperature rapid reduction and alloying of adjacent base metal ions. This phenomenon was utilized to develop a method for easily preparing high-entropy alloys and non-equilibrium alloy particles, designing catalysts that show high performance for CO_2 reduction, NOX decomposition, and hydrogen production from hydrogen carrier molecules.

References

1. K. Shun, H. Yamashita, et al., *Nature Comm.*, **2024**, 15, 6403.
2. H. J. Kim, H. Yamashiya, et al., *Adv. Mat.*, **2023**, 33, 2303994.
3. Y. Kuwahara, H. Yamashita, et al., *Chem. Sci.*, **2021**, 12, 9902.
4. K. Mori, H. Yamashita, et al., *Nature Comm.*, **2021**,12, 3884.
5. K. Mori, H. Yamashita, et al., *Nature Comm.*, **2019**, 10, 4094.
6. Y. Isaka, H. Yamashita et al., *Angew. Chem. Int. Ed.*, **2019**, 131, 5456.
7. H. Yamashita, et al., *Chem. Soc. Rev.*, **2018**, 47, 8072.
8. Y. Kuwahara, H. Yamashita, et al., *J. Am. Chem. Soc.*, **2018**,140, 9203.
9. K. Mori, H. Yamashita, et al., *J. Am. Chem. Soc.*, **2018**, 14, 08902.
10. H. Cheng, H. Yamashita, et al., *J. Am. Chem. Soc.*, **2016**,138, 9316.
11. K. Fuku, H. Yamashita, et al., *Angew. Chem. Int. Ed.*, **2013**, 52, 7446.
12. Y. Kuwahara, H. Yamashita, et al., *J. Am. Chem. Soc.*, **2012**, 134, 10757.

Dynamics in environmental catalysis: from surface coverages to reactor operation

Patrick Lott and Olaf Deutschmann

Karlsruhe Institute of Technology (KIT)

Abstract:

Dynamic operation, inherent to automotive emission control devices, can also enhance catalyst performance, reactivate aged catalysts, shift product composition, and create energy and material cycles. Linking active site processes with reactor scale enables applications in exhaust treatment, greenhouse gas reduction, chemical synthesis, and energy conversion.



Olaf Deutschmann, Chair of Chemical Technology at the Karlsruhe Institute of Technology (KIT), works on the development of climate- and environmentally-friendly chemical technologies including carbon capture, carbon-free chemical energy carriers, emission control, fuel and electrolysis cells, circular economy, and digitalization tools in catalysis and reaction engineering.

Environmental Catalysis in Industry: The Road Ahead

Pierdomenico BIASI[*,1], Raffaele OSTUNI[1], Alberto GARBUJO[1], Filippo BUTTIGNOL[1], Ludovica VILLANTIERI[1], Michal BIALKOWSKI[1],
[1]*CASALE SA, R&D Division, Via Giulio Pocobelli 6, 6900, Lugano, Switzerland.*
** p.biasi@casale.ch*

The green chemicals market is a growing segment of the broader chemical industry, with a global market value exceeding $100 billion in 2022 and projected to reach over $270 billion by 2032[1]. Environmental catalysis is increasingly recognized as a strategic enabler for industrial decarbonization and green chemical market, offering practical solutions to reduce emissions, improve energy efficiency, and meet evolving environmental regulations. From an industrial perspective, the adoption of catalytic technologies is not only a matter of environmental compliance but also a driver of operational competitiveness and long-term sustainability.

However, the shift toward renewable energy sources, characterized by their intermittent and variable output, introduces new operational challenges. Catalytic abatement systems, traditionally optimized for steady-state conditions, must now adapt to fluctuating loads, variable feedstock quality, and dynamic process conditions. This necessitates a rethinking of plant design, control strategies, and catalyst durability to ensure consistent performance and economic feasibility under non-continuous energy supply scenarios. Special attention is given also to the industrial deployment of green ammonia and green methanol technologies, which are reshaping the production landscape. Companies like Casale SA are leading the transition by integrating advanced catalytic systems into modular, scalable plant designs that accommodate renewable energy inputs. These solutions enable the production of green chemicals and/or energy carriers using hydrogen from electrolysis and captured CO_2, aligning with global decarbonization goals while maintaining industrial viability[2-4].

Chemical industry needs to actively respond to the challenges posed by the transition to low-carbon and renewable energy systems. Industrial players are increasingly adopting flexible process integration strategies that allow for dynamic operation under variable energy inputs, particularly from intermittent renewable sources like solar and wind. Advanced control systems and digital process monitoring are being implemented to maintain stability and efficiency in catalytic processes despite fluctuating conditions.

Moreover, the integration of hybrid energy-storage solutions—such as batteries, thermal storage, and hydrogen buffers—enables plants to decouple energy supply from demand, ensuring continuous operation of catalytic units. The industry is also innovating in the application of catalytic materials, not only through the design of new catalysts tailored for dynamic environments but also by repurposing traditional catalysts in novel configurations or under modified operating conditions to enhance resilience and performance.

Beyond technological adaptation, the chemical industry increasingly recognizes the pivotal influence of national and regional policies, as well as geopolitical and energy resource shifts, in shaping the pace and direction of catalytic technology adoption. The ongoing energy transition is prompting industries to reassess their strategies in light of evolving energy availability, infrastructure, and regulatory landscapes[5]. Policy instruments—including subsidies for green hydrogen, carbon pricing schemes, and stringent emissions regulations—are proving essential in steering industrial investment toward cleaner technologies. At the same time, growing market demand for low-carbon products, such as green ammonia and green methanol, is opening up new economic opportunities and reinforcing the strategic value of catalytic innovation as a core component of sustainable industrial development.

Ultimately, environmental catalysis is positioned not merely as a scientific advancement but as a strategic pillar of industrial transformation, enabling the chemical sector to align with global climate goals while maintaining competitiveness in a rapidly evolving energy landscape[6].

In conclusion, as the chemical industry navigates the complexities of the energy transition, environmental catalysis stands out as a critical enabler of both technological innovation and strategic resilience. Its integration into industrial systems not only supports the shift toward renewable energy and low-carbon production but also reinforces the sector's ability to remain competitive, adaptive, and aligned with global sustainability objectives. The convergence of market demand, policy support, and industrial innovation positions environmental catalysis as a cornerstone of the next generation of green chemical manufacturing.

References

1. https://www.gminsights.com/industry-analysis/green-ammonia-market
2. www.casale.ch
3. E. Filippi and C. Pizzolitto, *Catalysis Today* **2022**, *387*, 9-11
4. J. Rostroup-Nielsen, *Catalysis Today* **2023**, *423*, 113878
5. https://www.coherentmarketinsights.com/industry-reports/green-ammonia-market
6. C. Kong Chyong, E. Italiani and N. Kazantzis, Nature Communications **2025**, *16*, 766.

Acknowledgements

This activity is part of the AMAZE project. This research was funded by the CETPartnership, under the Joint Call 2023. The CETPartnership' s research projects are co-funded by the European Commission (Grant Agreement No. 101069750) and the national funding organizations listed on the CETPartnership website.

Plasma catalysis: Complex chemical and physical mechanisms

Annemie Bogaerts
Research group PLASMANT - Center of Excellence PLASMA
Department of Chemistry - University of Antwerp. Belgium.
** e-mail annemie.bogaerts@uantwerpen.be*

Short abstract:
Plasma catalysis is promising for green chemistry, as it combines the high reactivity of plasmas with the selective production of value-added products by catalysis. However, the underlying mechanisms are very complex and far from understood. Indeed, the catalyst affects the plasma behavior and the plasma species affect the catalytic reactions. In this lecture, the important research questions will be discussed, and examples will be given of how modeling can help to answer these questions.

Short CV:
Annemie Bogaerts was born in 1971 and obtained her PhD in Sciences in 1996 from UAntwerp, where she has been a full professor in physical chemistry since 2012, and head of the research group PLASMANT, which she founded from scratch and now counts ca. 50 members. Since 2005, she was the supervisor of 62 defended PhD theses. She published over 650 peer-reviewed papers since 1995 (and about 25 invited book chapters), with over 45,000 citations in Google Scholar (h-index = 106), and has about 265 plenary or invited lectures at international conferences or institutes since 1995. She is also co-inventor of 14 patent applications since 2019, and co-founder of 4 spin-off companies of her research group.

Zeolite catalysis for (bio)ethanol-to-hydrocarbons processes

Guido Busca*[,1], Elena Spennati[1], Paola Riani[2], Gabriella Garbarino[1]
[1]*University of Genova, DICCA, via Opera Pia 15, Genova, Italy.*
[2] *University of Genova, DCCI, via Dodecaneso 31, Genova, Italy.*
** Guido.Busca@unige.it*

Significance and Relevance

The behavior of protonic and cationic zeolites in the conversion of ethanol to hydrocarbons is described. Evidence is provided for the role of Brønsted acidity typical of zeolites in the ethanol dehydration step as well as in the ethylene oligomerization step(s) producing linear olefins. The role of the cavity in favoring cyclization of the hydrocarbon chain is also taken into account. The behavior of cationic species, such as Ni, Zn and Sn ions, in favoring aromatization is considered. Features of a promising process for producing renewable hydrocarbons from bioethanol are discussed.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion; Fundamental advances in understanding catalysis.
Preferred presentation: Oral > Short Oral > Poster.

Introduction and Motivations

In the near future, progressive defossilisation of energy production technologies and of chemical manufacturing is needed [1] and will certainly occur. However, hydrocarbons will still remain main chemical intermediates, to produce final products such as, e.g., lubricants, detergents and plastic materials [2]. Hydrocarbon-based biofuels will also be necessary for vehicles that cannot be full-electric or hydrogen-fueled, such as for large long-range shipping and aviation.[1] The zeolite-catalyzed (bio)ethanol to hydrocarbon is a potential new process allowing the renewable production of hydrocarbons. In this paper, mechanistic and compositional aspects for such catalysts are discussed.

Materials and Methods

Commercial H-FER, H-MFI, H-MOR, H-BEA, H-Y and H-USY zeolite samples have been used as the starting protonic zeolite catalysts. P, Fe, Ni, Sn and Zn containing catalysts were prepared by impregnation. Catalysts characterization was done using XRD, FE-SEM, skeletal FT-IR, UV-Vis-NIR techniques, as well as FT-IR spectroscopy of adsorbed CO and pyridine. Used catalysts were characterized by UV-Vis-NIR and DTA-TG techniques experiments. Catalytic experiments were performed at atmospheric pressure in a tubular flow reactor, with GC and GC-MS product analysis.

Results and Discussion

Protonic zeolites were found to be very active in converting ethanol into ethylene using relatively high space velocities.[3] The H-MOR sample is the most active, but the H-MFI samples with Si/Al_2 ratios 280 and 50 show higher reaction rates per Al ion, H-FER and faujasites show highest ethylene yield (99.9% at 573 K). At lower temperature and even higher space velocities, diethyl ether is formed with high yield (>70% at 453–473 K with H-BEA and H-MFI (50)). Only using MFI zeolite with relatively high Al content, and with mordenite to a much limited extend, at higher temperature (> 573 K) further conversion of ethylene is observed producing higher hydrocarbons, including aromatics (~29%). Formation of carbonaceous material is also observed over H-MFI, H-MOR and H-BEA. The catalytic activity is certainly primarily due to the strong Brønsted acidic character of the bridging hydroxy groups typical of protonic zeolite.[4] The different behavior of the protonic zeolite structures appears to be associated to confinement effects: in fact, medium-pore zeolites seem to favor the formation of aromatic hydrocarbons, and carbonaceous material.

Using H-ZSM5 (50) catalyst calcined at 700 K it was found that maximum over-conversion of ethylene to higher hydrocarbons was found at 673 K, while higher hydrocarbons activity was reduced at higher temperatures with increased ethylene production . This is likely due to thermodynamic

limitations on ethylene oligomerization at high temperature.[5] It was also found that, while the addition of phosphorus and iron decreases the ethylene over-conversion, the addition of 1 wt.% nickel increases the production of aromatics. Instead, the addition of 1 wt.% Zn can also have a positive effect on the production of aromatics, in particular benzene and xylenes.

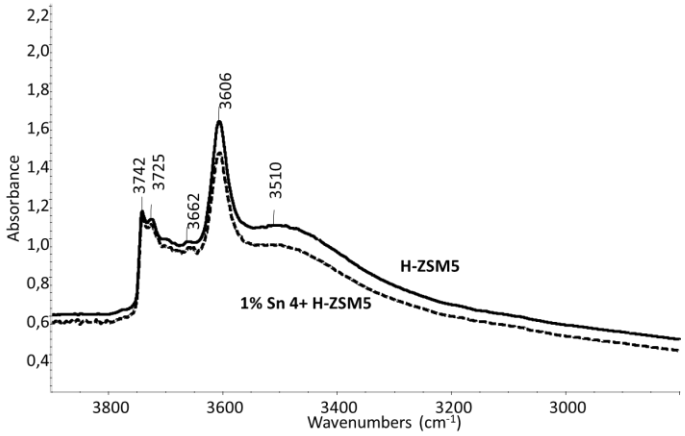


Figure 1. FT-IR spectra of the hydroxy group in protonic HZSM5 and on 1 Sn wt% -H-ZSM5 catalyst prepared using $SnCl_4 \cdot 5H_2O$ as precursor salt (outgassing at 773 K).

Indeed, to optimize higher hydrocarbons productivity, the addition of cations and optimization of space velocity are both needed. The addition of Sn^{4+} ions increase the conversion of ethanol to C6–C8 aromatic hydrocarbons up to a very interesting 34 % selectivity at 100 % ethanol conversion. In particular, the yield to aromatic-rich gasoline is over 40 % at 773 K and 2700 h^{-1} GHSV.[6]

Characterization data show that the most active Sn-ZSM5 catalyst is still an acid zeolite with limited addition of Lewis acidic Sn ions, part of which are likely introduced in the zeolite pores and part of which produce very small SnO_x nanoparticles on the external surface. In fact, the absorption band of the acidic bridging hydroxy groups is relatively markedly decreased by 1 wt% Sn addition (Fig. 1), likely due to cation exchange. Taking into account the already cited property of ZSM5 zeolite structure in favoring aromatization, the small amount of Brønsted acid sites in this high-silica zeolite, and the limited amount of Sn ions entering the pores, it seems likely that the production of aromatic hydrocarbons is favored by the coexistence of close couples of acids and Sn^{2+} sites (characterized by UV spectroscopy) in the zeolite. Since ethylene is the primary conversion product of ethanol over these catalysts, the aromatization process likely occurs on ethylene oligomeric chains. The role of Sn ions is mainly in favoring the cyclization and dehydrogenation of trimeric and tetrameric ethylene isomers produced by acid-catalyzed ethylene oligomerization.

These data suggest that Sn-doped H-ZSM5 zeolites can be proposed as catalysts for a (bio)ethanol to gasoline process, realized at 650-700 K and relatively low space velocities.

References

1. G. Busca, *Energies,* **2024**, *17,* 3565.
2. G. Busca, *Energies,* **2021**, *14*, 4061.
3. T. K. Phung, L. Proietti Hernandez, A. Lagazzo, G. Busca, *Appl. Catal. A Gen.,* ***2015****, 493*, 77-89
4. G. Busca, *Micropor. Mesopor. Mat.,* **2017***, 254,* 3-16.
5. T. K. Phung, R. Radikapratama, G. Garbarino, A. Lagazzo, P. Riani, G. Busca*, Fuel Proc. Techn.,* **2015***, 137,* 290-297.
6. E. Spennati, M. Iturrate, S. Bogni, A. Cosso, R. Millini, P. Riani, G. Busca, G. Garbarino, *Micropor. Mesopor. Mat.,* **2024,** *379,* 113284.

Revisiting Electrochemical Breakpoint Chlorination of Ammonium-Rich Wastewater: Reactive Chlorine Speciation on IrTaOx/TiO_2

Hyeonjeong Kim[1] and Kangwoo Cho[*,1]
[1]*Pohang University of Science and Technology (POSTECH), Division of Environmental Science and Engineering., 77 Cheongam-ro, Pohang, Republic of Korea.*
** kwcho1982@postech.ac.kr*

Significance and Relevance

Electrochemical breakpoint chlorination (EC-BC) offers a promising method for ammonia-nitrogen (N) removal, though the roles of reactive chlorine species (RCS) are not fully understood. This study explored RCS speciation on an IrTaOx/TiO_2 anode, which demonstrated superior RCS generation influenced by pH, current density, and chloride concentration. Our findings demonstrated that dichlorine radical anion ($Cl_2^{\cdot-}$), previously underexplored, plays a critical role in degrading ammonia-N in wastewater into nitrogen gas (N_2). Acidic pH favored Cl_2-· and chlorine evolution, while alkaline conditions enhanced NH_3 speciation, improving removal rates. We also tested the EC-BC for treatment of ammonia-rich alkaline industrial wastewater, focusing on the cathodic scale formation and operation control strategy.

Preferred and 2nd choice for the topic: Water treatment
Preferred presentation: Oral preferred

Introduction and Motivations

Traditional biological wastewater treatment plants are ineffective for high-strength N and recalcitrant wastewater, such as that from industries, due to a low carbon-to-nitrogen ratios and extended retention time (on the order of several days) requirement. In this context, the EC-BC offers a promising alternative as it can handle high N loads within a few hours by controlling the production of RCS, including chlorine radicals [1]. However, the role of RCS species on the efficiency of EC-BC along with the effects of operating parameters remains being insufficiently explored[1,2]. This study tackles this research bottleneck, while proves the practical applicability of the EC-BC to deal with industrial wastewater with variable pHs.

Materials and Methods

The EC-BC experiments were conducted using a three-electrode system consisting of an IrTaO$_x$/TiO_2 anode, a SUS304 cathode, and an Ag/AgCl (3M NaCl) reference electrode, with a current density of 200 A m^{-2} unless otherwise specified. The reactions were carried out in a solution containing 100 mM NaCl and 50 mM $(NH_4)_2SO_4$, with the pH adjusted using NaOH and H_2PO_4. Radical steady-state concentrations ($[radical]_{ss}$) and scavenging tests in the EC-BC system were conducted using benzoic acid (BA, 50 µM), para-chlorobenzoic acid (p-CBA, 50 µM), and 1,4-dimethoxybenzene (DMOB, 500 µM) as probe compounds for ·OH, Cl·, and ClO·, as well as carbamazepine (CBZ, 500 µM) to scavenge ·OH, Cl·, ClO·, and $Cl_2^{\cdot-}$.

Results and Discussion

Fig. 1a demonstrates that ClER on IrTaO$_x$/TiO_2 anode achieves efficient EC-BC, resulting in complete conversion of ammonia to N_2 gas. However, Fig. 1b reveals that the ammonia-N degradation rate as a function of pH (pink line) has contrasting trends against a chemical breakpoint chlorination (C-BC, blue line). Notably, despite the limitation under acidic conditions, with predominant free chlorine as HOCl and ammonia-N as NH_4^+ leading to a low intrinsic bimolecular rate constant,[3] the EC-BC system exhibited the highest ammonia-N degradation rate under the acidic pH. This suggests the presence of critical factors governing the EC-BC system that are absent in the C-BC system. Chlorine radical species are critical for ammonia degradation in electrochemical advanced oxidation processes (E-AOPs) during ClER. These radicals are distinctly generated in the EC-BC system but are absent in conventional C-BC system. We systematically investigated not only OH·, Cl·, ClO· but also $Cl_2^{\cdot-}$, which have been largely

overlooked in the context of ammonia degradation within E-AOPs due to their relatively low bimolecular rate constant with ammonia (3.5×10^5 M^{-1} s^{-1}). Our results demonstrate that $Cl_2^{\cdot-}$ plays a crucial role in the EC-BC system, with its concentration being several orders of magnitude higher than that of other radical species across all pH levels (Fig. 1c). The concentration of $Cl_2^{\cdot-}$ is particularly elevated under acidic conditions, as confirmed by scavenging tests (Fig 1d), which indicates that $Cl_2^{\cdot-}$ is predominantly involved in ammonia degradation. This enhanced generation in acidic environments can be attributed to an elevated equilibrium potential of the competing OER[4]. The increased efficiency of ClER promotes higher Cl· production, shifting the equilibrium between Cl· and $Cl_2^{\cdot-}$ (as described in Eq. 1), thus establishing a regime where $Cl_2^{\cdot-}$ dominates. Additionally, Fig. 2 shows that the concentration of $Cl_2^{\cdot-}$ increases with higher initial chloride concentrations and current density, further supporting this mechanistic insight.

$$= \frac{[\cdot][^-]}{[_2^{\cdot-}]} \qquad \text{(Eq. 1)}$$

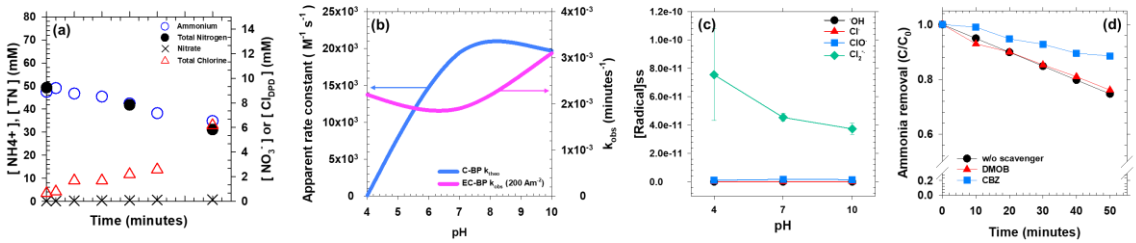


Figure 1. (a) Ammonia-N conversion to N_2 during EC-BC through ClER on an $IrTaO_x/TiO_2$ in pH 7, (b) Comparison of ammonia degradation rate between C-BC and EC-BC depending on pH, (c) $[radical]_{ss}$ depending on pH in EC-BC system and (d) Radical scavenging test in EC-BC system at pH 4.

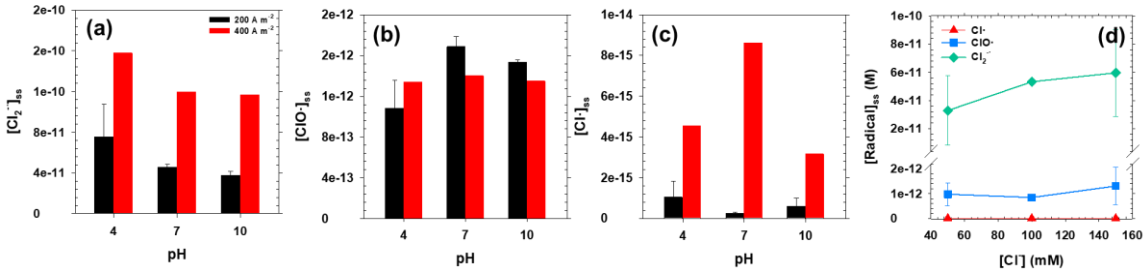


Figure 2. Influence of current density on $[radical]_{ss}$ of (a) $Cl_2^{\cdot-}$, (b) ClO·, and (c) Cl· and (d) impact of initial chloride concentration on the $[radical]_{ss}$ during EC-BC in pH 4.

The EC-BC system via ClER on $IrTaOx/TiO_2$ electrocatalyst offers a promising alternative for the denitrification of acidic wastewater, which poses challenges for conventional C-BC methods, owing to the efficient generation of $Cl_2^{\cdot-}$. In addition, the highest efficiency of EC-BC was obtained in an alkaline pH, which could be utilized to handle an ammonia-N rich, alkaline industrial wastewater.

References

1. Li. Q, Liu. GH, *Science of The Total Environment* **2023**, *896*, 165169.
2. Huang X, Zhang Y, *Chemical Engineering Journal* **2020**, *792*, 123695.
3. Qiang Z, Adams CD, *Environmental science & technology* **2004,** *38*, 1435
4. Krishtalik LI., *Electrochimica Acta* **1981,** *26*, 329

Acknowledgements

This work was supported by National Research Foundation of Korea (NRF-2022R1A2C4001228)

Upgrading of plastic pyrolysis oil model compounds over ZSM5-based catalysts: Effect of reactor type and operating variables

S-A. Andrianos[1], P. Soldatos[2], K. Triantafyllidis[2], A.A. Lemonidou[1*]
[1]School of Chemical Engineering, [2]School of Chemistry,
Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece
[*]alemonidou@cheng.auth.g

Significance and Relevance

The heavy fraction of plastic pyrolysis oil can be efficiently upgraded at mild conditions over ZSM5-based catalysts yielding a liquid product with optimum composition in naphtha range as shown by the tests conducted specifically in batch reactors with n-hexadecane and 1-hexadecene as model compounds. The deposition of 2.15wt% Ru metal on ZSM5 proved beneficial for the activity, especially under hydrogen atmosphere.

Preferred topic: 1st Circular economy, 2nd Sustainable and clean energy production and transport
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Plastic recycling remains a challenge, with a substantial portion of recycled plastics ending up in landfills or polluting oceans. Several approaches for plastic recycling are under development nowadays with the more technologically mature that of mechanical recycling. However, plastics obtained from mechanical recycling methods are of lower quality and are characterized by higher unit production costs compared to primary plastics[1]. An alternative way of managing plastic waste is chemical recycling, with the pyrolysis process playing the major role. Pyrolysis can be a viable option as it can convert all types of plastics into a product mixture which can be either used as fuel or as source of monomers. However, the quality of the resulting oil is unsuitable to be directly used in existing steam cracking units necessitating selective upgrading[2]. Thermal upgrading hinders the conversion of heavy hydrocarbons due to the random decomposition mechanism and therefore the use of catalysts is recommended. It is well known that cracking reactions necessitate acidic functionalities on the catalyst surface while the presence of metals can further affect the mechanistic pathways[3]. This study aims to catalytically upgrade pyrolysis products by selectively decomposing the heavy fraction of pyrolysis oil into naphtha-range hydrocarbons. Two model compounds, namely a paraffin and an olefin with 16 C-atoms representing the light fronts of the heavy oil fraction, are employed in the study. The effect of phase (liquid or gaseous) under which the pyrolysis reactions proceed is explored by employing high pressure batch and atmospheric pressure fixed bed reactors and ZSM5-based catalysts.

Materials and Methods

The catalysts used were the ZSM5 (Si/Al=25) and the one promoted with 2.15 wt% Ru. The deposition of Ru was performed following the wet impregnation method with subsequent drying and calcination at 500°C for 3h. The experiments were conducted using batch and fixed bed reactors. The tests in the batch reactor were conducted at 300°C, high initial pressure 20bar (in N_2 or H_2 atmosphere) to ensure that the reactions proceed in the liquid phase while that of fixed bed at atmospheric pressure and temperature ranging from 250 to 350°C and W/F 0,4-0.9 $g_{cat}/mol_{C16}.h$. The analysis of gaseous and liquid products was performed employing four gas chromatographs equipped with suitable columns and detectors.

Results and Discussion

The conversion of n-Hexadecane at 300°C under batch conditions highly depends on the type of catalyst (Ru promoted or non-promoted ZSM5) and the gaseous atmosphere (N_2 or H_2) used. The presence of Ru and the reducing atmosphere favor the feed conversion which reaches 62wt% after 2h

of testing (Fig 1a). The liquid products formed are highly paraffinic (n- and i-) in the range of C5-C11 and comprise ~90wt% of the total products (Fig. 1b). The gaseous products consist mostly of C3 and C4 with dominance of propane. The long residence time of the intermediates formed most likely enhances the H-transfer reactions leading thus to paraffinic compounds[4]. The liquid/gas selectivity remains almost constant irrespective of the catalyst and the atmosphere. Deposition of intermediates and coke like compounds was detected which however do not surpass 0.3wt% of the feed.

In the fixed-bed reactor operating at atmospheric pressure, reactions occur in gaseous phase. Increasing temperature from 250 to 350°C enhances total conversion to over 95 wt% at 350°C and 0.15 s residence time, especially in the presence of Ru/ZSM5 catalyst. Pyrolysis in the gas phase boosts cracking increasing selectivity towards gas products (C_3-C_4) from 40 to 60 wt% at the expense of liquid products which comprise of light hydrocarbons (C_5-C_7). Residence time, despite being very short (0.078-0.15s), linearly increases total conversion and productivity without changing the gas/liquids selectivity. The gaseous and liquid products formed are rich in alkenes with mostly iso and normal olefins accounting for 60 wt% of the products.

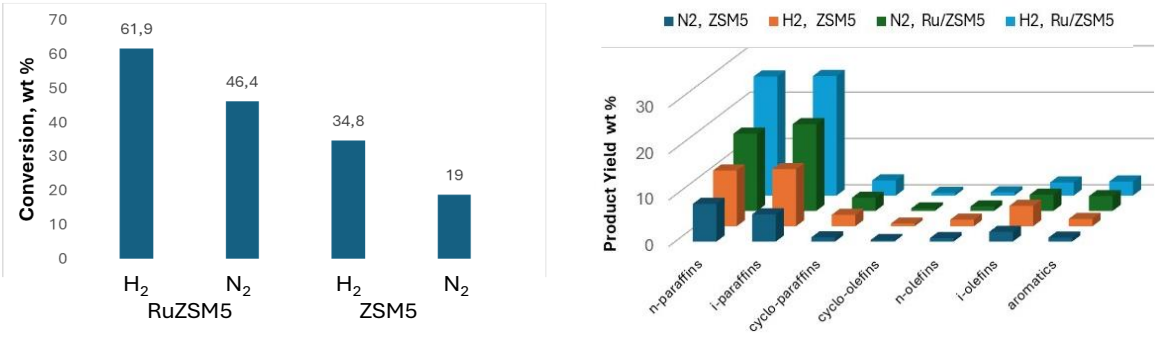


Figure 1 n-Hexadecane pyrolysis in a batch reactor at 300°C and 20 bar pressure as a function of catalyst and gaseous atmosphere a) wt% nC16 conversion b) wt% product yield distributed according to PIONA composition

Upgrading of plastic pyrolysis oil can effectively proceed under relatively low temperature around 300°C over ZSM5 based catalysts. The reactor type and the pressure, which determines the gaseous or liquid phase in which the reactions take place, have the main role in product selectivity. Hydrocarbons in the desired range of naphtha (90wt% of the products) with minimum olefinic content even in the absence of H_2 in the gas phase, are formed under batch conditions. The presence of Ru affects mostly the activity. In contrast, in the fixed bed reactor tests, n-Hexadecane, at similar temperatures, is almost fully converted to a hydrocarbon mixture C3-C7 with gases/liquids ~50% (wt) with olefins being the main constituents. Research activities are ongoing with 1-Hexadecene, as model compound, to explore the effect of the same parameters on catalytic cracking of the olefinic hydrocarbon.

References

1. D. P. Serrano, J. Aguado, J. M. Escola, *ACS Catalysis* **2012,** *2* (9), 1924-1941.
2. M. Kusenberg, A. Eschenbacher, L. Delva, S. De Meester, E. Delikonstantis, G. D. Stefanidis, K. Ragaert, K.M. Van Geem, *Fuel Processing Technology* **2022,** 238, 107474
3. J. E. Rorrer, A. M. Ebrahim, Y. Questell-Santiago, J. Zhu, C. Troyano-Valls, S. R. Tassone, C. J. Beckham, Y. Román-Leshkov, *ACS Catalysis* **2022,** *12* (22), 13969-13979
4. W.T. Lee, A. Van Muyden, F.D. Bobbink, M.D. Mensi, J.R. Carullo, P.J. Dyson, *Nature Comm.* **2022** 13,4850

Acknowledgements

Financial support by the EU project ELECTRO (Horizon-CL4-2021-Twin-Transition-01, grant agreement 101058412) is gratefully acknowledged.

Porous Macroligands for Heterogenized Photocatalytic Solar Fuel Production

Jérôme CANIVET*, Emilien CHAIGNE--TARLOTIN, Elsje Alessandra QUADRELLI
Université Claude Bernard Lyon 1, CNRS, IRCELYON - UMR 5256, 2 Avenue Albert Einstein, 69626 Villeurbanne Cedex, France
** jerome.canivet@ircelyon.univ-lyon1.fr*

Significance and Relevance

These findings highlight the promise of developing fully heterogeneous photosystems that use solar light as the sole energy source to convert CO_2, a major greenhouse gas, into valuable solar fuel. Recent efforts have focused on applying insights from molecular science to design heterogenized photosystems that leverage the structured framework of porous materials, including plasticity in a device-oriented perspective. With collaborative advances from both molecular and materials science, breakthrough photosystems using porous macroligands for heterogenized molecular catalysis for efficient carbon-based solar fuel production are likely to emerge in the near future.

Preferred and 2nd choice for the topic:

1. Photocatalysis and photoelectrocatalytic approaches, solar energy utilization
2. CO2 utilization and recycling

Preferred presentation: Oral preferred

Introduction and Motivations

Photocatalytic CO_2 reduction reactions have gained enormous interest, as they offer sustainable routes to provide renewable fuels and small building blocks for chemicals. However, efficient, selective and long-term active photocatalysts and well-understood molecular structures of the active sites are still scarce. A fruitful strategy in the design of molecularly-defined heterogeneous catalysts is to immobilize isolated active sites within a hosting framework.

The integration of the catalytically active centers into a solid support without loss of performance compared to the homogeneous analog is still a major challenge.

To change the paradigm of molecular catalytic processes for fine chemical synthesis and green fuel production, we introduced recently the concept of solid porous macroligand for heterogenized molecular catalysis.[1] Having molecularly-defined active sites, porous macroligands have been found to drive the activity and the selectivity of heterogenized catalytic processes on a similar way as molecular ligands but with the advantage of the structuration in a three-dimensional framework and the confinement within a porous nanospace.[2]

Results and Discussion

Heterogeneous catalysis brings various advantages compared to homogeneous catalysis such as recyclability and easy separation of the product from the catalyst. Heterogenization of molecular catalyst can be performed using solids acting as macroligands for site-isolated molecular complex. We already demonstrated that fully heterogenous systems based on porous organic polymer macroligand POP displayed high productivity and stability over the time for the CO2 to formic acid photoreduction (Figure 1).

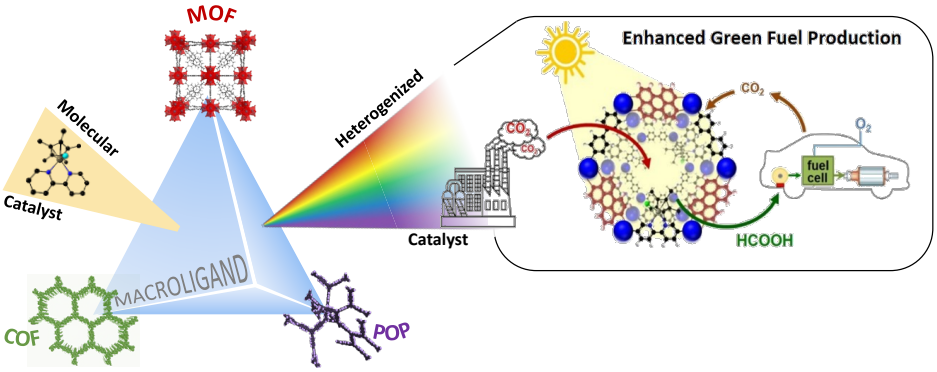


Figure 1 Porous hybrid solids as macroligands for the photocatalytic CO_2 conversion.

Aiming at increasing the sustainability of the photocatalysts synthesis, we moved from the previously reported palladium catalyzed macroligand synthesis to radical polymerization. Starting from vinylated monomers, this new synthetic strategy would bring flexibility into the POP macroligand along with new optical and electronic properties. The goal would be to build full heterogeneous systems, based on the same composition as the previous POP generation,[3,4] with PS and coordination site, acting as macroligands for the catalyst.

Preliminary tests were conducted on the Rh catalyst heterogenized within N-POP material and used with an external photosensitizer.[5]

In this work, an organic photosensitizer is successfully integrated within a porous organic polymer (POP) structure, preserving its photophysical and photocatalytic properties. This innovation aims to create all-in-one heterogeneous photocatalysts with both organic dyes and a molecular Rh catalyst as single sites in a non-conjugated porous matrix. The POP, constructed around perylene or polythiophene units, efficiently supports light harvesting and electron-hole generation. The inclusion of bipyridine co-monomers enables the coordination of organometallic active site as isolated single-site molecular catalysts for CO_2 reduction, producing formic acid as the sole carbon-based product. This highlights the synthetic versatility of POPs as porous macroligands, opening pathways for more sustainable molecular catalytic processes and solar fuel production. The results presented remain so far unpublished.

References

1. Wisser et al., *ChemCatchem* **2020**, *12*, 1270-1275.
2. Rajapaksha et al., *Chem. Soc. Rev.*, **2023**, *52*, 8059-8076.
3. Fávaro et al., *ChemCatChem* **2023**, *15*, e202300197.
4. Wisser et al., *Angew. Chem. Int. Ed.* **2020**, *59* , 5116–5122.
5. Newar et al., *Adv. Energy sustainabilit Res.*, **2024**, 5, 2300209.

Acknowledgements

This work has benefited from French State aid managed by the Agence Nationale de la Recherche under France 2030 plan, bearing the reference code ANR-22-PESP-0010 : Projet ciblé "POWERCO2" within the PEPR project SPLEEN.

Room temperature reduction of NO without reductants on iron Metal-Organic Frameworks

Marco DATURI[*,1], Vanessa BLASIN-AUBÉ[1], Ji Wong YOON[1,2], Philippe BAZIN[1], Alexandre VIMONT[1], Jong-San CHANG[1,2], Stefan WUTTKE[1,4,5], Christian SERRE[5]

[1] *Université de Caen Normandie, ENSICAEN, CNRS, LCS, Laboratoire Catalyse et Spectrochimie, 14000 Caen, France.*

[2] *Catalysis Center for Molecular Engineering, Korea Research Institute of Chemical Technology (KRICT); Jang-dong 100, Yuseong, Daejeon, 305-600, South Korea.*

[3] *Department of Chemistry, Sungkyunkwan University; Suwon, 440-476, South Korea*

[4] *Ikerbasque, Basque Foundation for Science, Bilbao 48009, Spain & BCMaterials, UPV/EHU, Science Park, Leioa 48940, Spain*

[5] *Institute of Porous Materials from Paris, ENS, ESPCI Paris, CNRS, PSL University, Paris 75005, France*

** marco.daturi@unicaen.fr*

Significance and Relevance

For the first time, using theoretical modelling, material design, state-of-the-art investigation methods and mimicking enzymes, we have found that selected porous hybrid iron(II/III) based MOF materials are able to decompose NOx, at room temperature, in the presence of water and oxygen, into N_2 and O_2 and without reducing agents. These materials, stable up to 300°C, can be easily upscaled and wash-coated for possible future industrial applications. This paves the way to the development of new highly sustainable heterogeneous catalysts to improve air quality.

Preferred and 2nd choice for the topic: Air cleaning and combustion; Automotive and stationary emission control

Preferred presentation: Oral only

Introduction and Motivations

Air pollution is an epochal concern, and is linked to combustion processes, leading to the emission of nitrogen oxides (NOx), which constitutes a critical environmental problem, and it can affect severely human health.[1] At ambient temperature and pressure, NOx decomposition is thermodynamically favoured; however, this process is kinetically inhibited, owing to a high activation energy. To date, no reported heterogenous catalyst possesses the required properties to lower the activation energy of this process without the help of co-reacting agents and high temperature. Nature resolves the denitrification problem with an assortment of different iron and copper based metalloenzymes,[2,3] that sequentially reduce nitrate to dinitrogen via nitrogen oxide intermediates, e.g., nitrate reductase, nitrite reductase (NIR), nitric oxide reductase (NOR) and nitrous oxide reductase. However, the latter ones cannot be applied directly for the purification of polluted gases, as these molecular moieties can be activated only in liquid phase. Catalysts that are intended to mimic enzyme mechanisms should therefore have a similar configuration.

Materials and Methods

MOF samples were hydro/solvothermally prepared, then characterized by XRD, BET, FTIR, SEM, HRTEM, and *in situ* XANES. The cluster model calculations were carried out based on first principles density functional theory (DFT) calculations, implemented in DMol^3 and Vienna Ab initio Simulation Package (VASP). Mechanistic insights were obtained via *operando* IR investigations.

Results and Discussion

The mesoporous iron(III) trimesate MIL-100(Fe) is a hydrothermally stable MOF built up from oxo-centred trimers of iron(III) octahedra interconnected by 1,3,5-benzene tricarboxylate linkers giving rise to a mesoporous zeo-type architecture (Fig. 1).[4] IR *in situ* analyses show that, after synthesis, this material presents only accessible Fe(III) sites. After activation in Ar at 250°C for 5h, the samples show the presence of Fe(II) sites as well, in the proportion of one Fe(II) per trimer. Under a gas reaction flow

typically containing 1000 ppm NO, 10% O_2, and 1% H_2O at room temperature, the untreated sample showed a partial conversion of NO into NO_2, whereas the sample containing mixed Fe(II)/Fe(III) sites showed a steady conversion of NO into stoichiometric amounts of N_2 and O_2, depending on the space velocity (for example, 34% at GHSV = 15000 h^{-1}). Experiments using isotopically labelled $^{15}N^{18}O$ confirmed the nitrogen and oxygen yield. Additionally, it was discovered that the presence of oxygen and water vapour in the flow is a necessary condition to induce the NO decomposition. EXAFS/XANES Synchrotron analysis, using similar *operando* conditions, confirmed the presence of Fe(II)/Fe(III) mixed sites as being essential for NO conversion. Further *operando* experiments allowed to propose a reaction mechanism dealing with the partial oxidation of NO into NO_2 (and a concomitant reduction of a Fe(III) into a (Fe(II) site), the formation of a N_2O_3 intermediate, followed by its decomposition into N_2O and O_2, with the nitrogen protoxide oxidising back the Fe(II) site into Fe(III) and providing the emission of dinitrogen.

This discovery allowed to find, for the first time, a catalyst able to decompose NO at room temperature and in the presence of oxygen and water, without the assistance of a reducing species. This represents a leap forward in the comprehension of the deNOx mechanism, and allows to bridge the gap between heterogeneous and enzymatic catalysis. Moreover, different complex problems in catalysis could be solved, in perspective, using a similar approach based on enzyme mimicking via highly tailorable materials as MOFs. Finally, this kind of catalysts can be envisaged to be used for air purification in specific confined polluted ambient, such as underground parking, tunnels, factories, cockpits, in-house etc.[5]

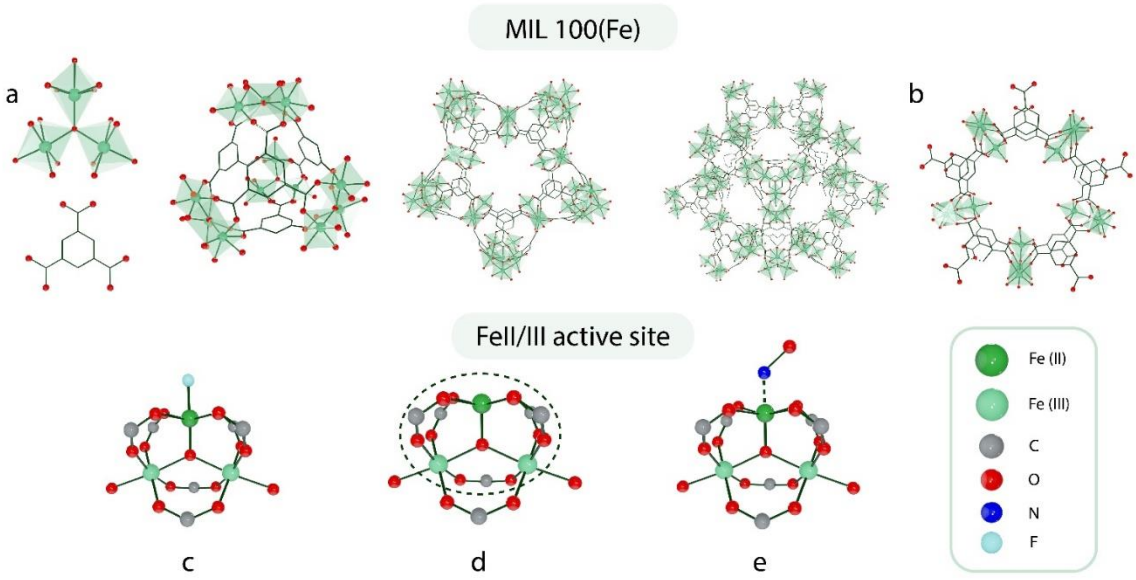


Figure 1: Schematic representation of the iron trimesate MIL-100(Fe) and the binding of NO over the iron metal sites. (a) A mesoporous cage of MIL-100(Fe). (b) A porous cage of MIL-100(Fe). (c) View of one hydrated trimer of iron(III) octahedra. (d) One dehydrated and defluorinated trimer of iron(II, III) octahedra. (e) Coordination of one NO molecule over one Fe(II)/Fe(III) model cluster.

References

1. E. Samoli *et al*., Eur. Respir. J. 2006, 27, 1129.
2. B. A. Averill, Chem. Rev. 1996, 96, 2951.
3. I.M. Wasser, et al., Chem. Rev. 2002, 102, 1201.
4. P. Horcajada *et al*., Chem. Commun. 2007, 2820.
5. M. Daturi *et al*., Adv. Mater. 2024, 2403053.

Generation of oxide surface patches promoting H-spillover in Ru/(TiO_x)MnO catalysts enables CO_2 reduction to CO

Hui Kang,[1] Shiyan Li,[1] Jun Ma,[1] Xuxu Zhai,[1] Siglinda Perathoner,[2] Gabriele Centi,[2] Yuefeng Liu [*,1]

[1] *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China*

[2] *Department of ChiBioFarAm, University of Messina, Messina 98166, Italy*

** e-mail: yuefeng.liu@dicp.ac.cn*

Gas-driven reconstruction is an attractive and precise strategy to tune sub-nano even atomic structure for catalysts. The migration of reducible metal oxides (especially for TiO_2) to the surface of metal nanoparticles can inhibit the sintering but has a strong negative impact on the catalytic activity. Herein, we reveal the *in-situ* creation of TiO_x patches over the MnO support to generate effective transport channels for H-spillover to transport it from the Ru nanoparticles to the MnO sites responsible for reducing CO_2 to CO, a key reaction for CO_2 conversion to high-value chemicals. The Ru/(TiO_x)MnO (Ru/Ti/Mn) catalyst shows a 3.3-fold increase in reverse water gas shift (RWGS) performance compared with conventional Ru/MnO_x catalysts (Fig. 1a) due to the enhcanced H-spillover (Fig. 1b). Through a combination of physicochemical methods, including *in-situ* studies, catalytic and kinetic data, and theoretical modelling, we demonstrate that the oxide-oxide interfaces are spontaneously generated during reductive treatment in H_2 at temperatures below 500 °C and are responsible for the increased activity (Fig. 1c). The results open new perspectives for the design of novel selective hydrogenation catalysts via the *in-situ* creation of oxide-oxide interfaces acting as H species transport channels.

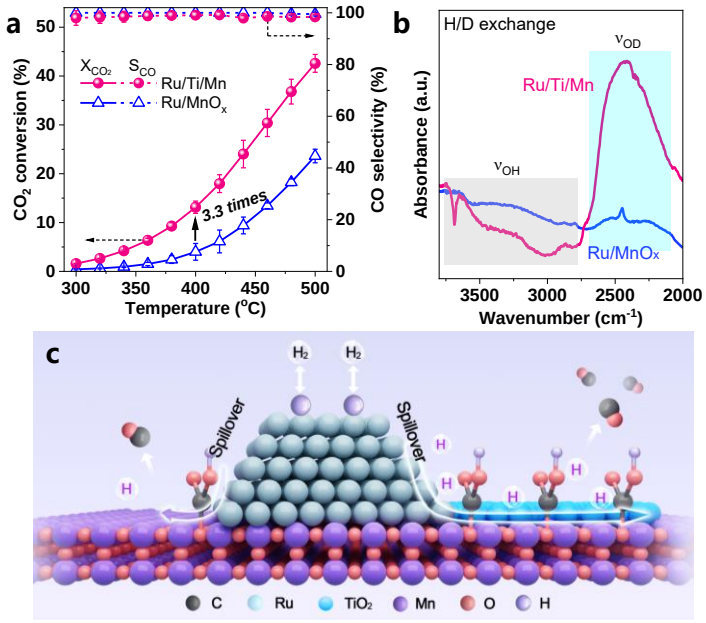


Figure 1. a, CO_2 hydrogenation performance for Ru/MnOx and RuTiMn. **b,** H-D exchange DRIFTs and **c,** TiO_2/MnO interface as effective H transport channel accelerate CO_2 to CO.

References

1. M. Monai, et al., Science, 2023, 380. 644-651.
2. H. Kang, et al. Nature Catalysis, 2023, 6,1062-1072.

Acknowledgements

This work was financially supported by the NSFC of China (22172161, 21972140 and 22472168) and LiaoNing Revitalization Talents Program (XLYC1907053).

Next, the effect support on catalytic performance of clusters was studied. When using iron oxide as the support for Cu_4 clusters[4], thanks the symbiotic interplay between the two metal components, the catalysts selectivity with temperature shifted between the formation of methanol (Fig1b and C2 hydrocarbons, while boosting methanol production 4-fold in comparison with the alumina support).

To further leverage the effect of the support and its morphology on performance, the studies continued with Cu_4 and Cu_{12} clusters supported on amorphous alumina and nanocrystalline zirconia[5], with selectivity switched fully to the formation of methane peaking at 375 °C. Cluster supported on nanocrystalline zirconia showcased a 2-fold increase in activity, confirming the role of surface morphology (i.e. bod length and structure) on the performance of the clusters, presumably via altered structure of clusters due their epitaxial wetting of the surface.

The aforementioned results demonstrate the available controls in efficient CO_2 conversion, of both activity and selectivity, by cluster size and cluster-surface interactions. For the conclusion of the paper, recent results on further optimizing the process of CO2 conversion on subnanometer clusters, results obtained by utilizing and additional tuning know, extension to bimetallic clusters of CuPd will be presented, changing the composition of 4- and 5-atom CuPd clusters one atom a time, following predictions from theory.[6]

References

1. Centi, G.; Quadrelli, E. A.; Perathoner, S. Catalysis for CO_2 Conversion: A Key Technology for Rapid Introduction of Renewable Energy in the Value Chain of Chemical Industries. *Energy Environ. Sci.* **2013**, *6* (6), 1711.
2. Liu, C.; Yang, B.; Tyo, E.; Seifert, S.; DeBartolo, J.; von Issendorff, B.; Zapol, P.; Vajda, S.; Curtiss, L. A. Carbon Dioxide Conversion to Methanol over Size-Selected Cu_4 Clusters at Low Pressures. *Journal of the American Chemical Society* **2015**, *137* (27), 8676-8679. DOI: 10.1021/jacs.5b03668.
3. Yang, B.; Liu, C.; Halder, A.; Tyo, E. C.; Martinson, A. B. F.; Seifert, S.; Zapol, P.; Curtiss, L. A.; Vajda, S. Copper Cluster Size Effect in Methanol Synthesis from CO_2. *J. Phys. Chem. C* **2017**, *121* (19), 10406-10412. DOI: 10.1021/acs.jpcc.7b01835.
4. Yang, B.; Yu, X.; Halder, A.; Zhang, X.; Zhou, X.; Mannie, G. J. A.; Tyo, E. C.; Pellin, M. J.; Seifert, S.; Su, D.; Vajda, S. Dynamic Interplay between Copper tetramers and Iron Oxide Boosting CO_2 Conversion to Methanol and Hydrocarbons under Mild Conditions. *ACS Sustainable Chemistry & Engineering* **2019**. DOI: 10.1021/acssuschemeng.9b01561.
5. Halder, A.; Lenardi, C.; Timoshenko, J.; Mravak, A.; Yang, B.; Kolipaka, L. K.; Piazzoni, C.; Seifert, S.; Bonačić-Koutecký, V.; Frenkel, A. I.; Milani, P.; Vajda, S. CO_2 Methanation on Cu-Cluster Decorated Zirconia Supports with Different Morphology: A Combined Experimental In Situ GIXANES/GISAXS, Ex Situ XPS and Theoretical DFT Study. *ACS Catalysis* **2021**, *11* (10), 6210-6224. DOI: 10.1021/acscatal.0c05029.
6. Mravak, A.; Vajda, S.; Bonacic-Koutecky, V. Mechanism of Catalytic CO_2 Hydrogenation to Methane and Methanol Using a Bimetallic Cu_3Pd Cluster at a Zirconia Support. *J Phys Chem C Nanomater Interfaces* **2022**, *126* (43), 18306-18312. DOI: 10.1021/acs.jpcc.2c04921.

Acknowledgements

S.V acknowledges the initial support by the US Department of Energy, Basic Energy Sciences, followed by funding by the European Union under Horizon Europe (project 101079142).

Bridging the materials space in CO_2 conversion using model subnanometer clusters and nanometer size particles synthesized by wet chemistry

Stefan VAJDA

Department of Nanocatalysis, J. Heyrovsky Institute of Physical Chemistry., Czech Academy of Sciences, Dolejškova 2155/3, 18223 Prague, Czech Republic

Significance and Relevance

This paper addresses the control of activity and selectivity in the conversion of carbon dioxide by using model catalysts made of a handful of atoms fabricated by physical deposition of clusters from molecular beams in vacuum and "real" catalysts prepared using wet chemical routes In model catalysts, the tuning of performance is achieved *via* changing the size- and atomic composition of subnanometer clusters along with the composition and crystallinity of the support. In the "real" catalysts variations in the morphology of the support at longer scales and the size of the nanoclusters are leveraged to switch selectivity between products like methanol. methane, carbon monoxide and C1+ hydrocarbons.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling; CO2 utilization and recycling
Preferred presentation: Oral only

Introduction and Motivations

Gas-phase catalytic conversion of carbon dioxide[1] with hydrogen, is addressed under mild pressure and temperature conditions, with the goal to identify efficient catalysts with their performance tunable between various C1 and C2+ products, while bridging the materials gap stating off with a single atom.

Materials and Methods

As models of the catalytic active center, small monometallic clusters of copper consisting of a handful of atoms were used, generated ligand-free in a magnetron sputtering source and after mass selection of size with atomic precision deposited on supports made of amorphous alumina and iron oxide, as well as amorphous and nanocrystalline zirconia. The thin, 3 monolayer to 1 nm amorphous supports films were prepared by atomic layer deposition, the nanocrystalline zirconia one in molecular beams. The catalysts were then tested under 1.1 atm pressure, with CO_2 and hydrogen seeded in He. The nanoscale copper catalysts dispersed on iron oxide particles were prepared by varying the synthesis process to achieve a spectrum in copper particle sizes and the morphology of the iron oxide particles serving as support.

Results and Discussion

In the first part of the presentation, the performance of model in their size- and composition dependent subnanometer clusters will be discussed. As an example, Cu clusters of three sizes, made of 3, 4 and 20 atoms deposited on alumina film were investiga-ted, revealing Cu_4 cluster as the most potent one. Next, the effect support on performance

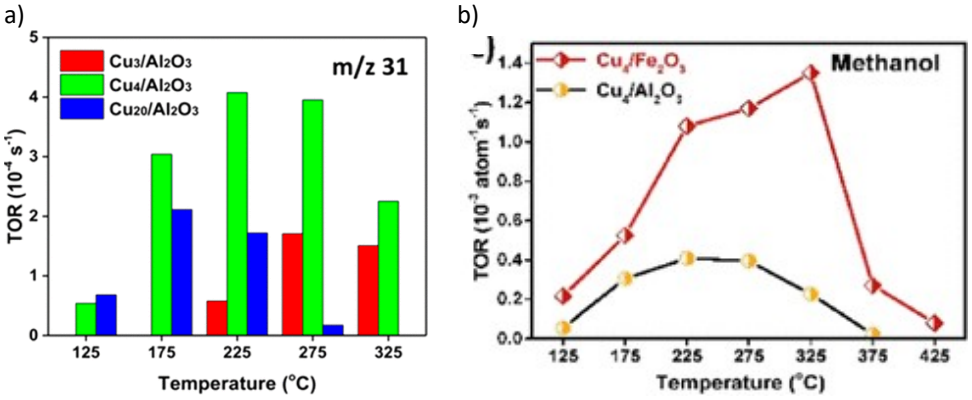


Figure 1 (a) Cu cluster size-dependent activity in methanol formation; (b) increase of methanol formation for Cu_4 clusters supported on iron oxide.

of clusters was studied. When using iron oxide as the support for Cu_4 clusters[4], thanks the symbiotic interplay between the two metal components, the selectivity with temperature shifted between the formation of methanol (Fig1b) and C2 hydrocarbons, while boosting methanol production 4-fold in comparison with the alumina support.

To further leverage the effect of the support and its morphology on performance, the studies continued with Cu_4 and Cu_{12} clusters supported on amorphous alumina and nanocrystalline zirconia[5], with selectivity switched fully to the formation of methane peaking at 375 °C. Clusters supported on nanocrystalline zirconia showcased a 2-fold increase in activity, confirming the role of surface morphology (i.e. bod length and structure) on the performance of the clusters, presumably via altered structure of clusters due their epitaxial wetting of the surface.

The aforementioned results which demonstrate the available controls for achieving efficient CO_2 conversion by subnanometer clusters by cluster size and through cluster-surface interactions, an outlook for the use of another control knob will be demonstrated, namely by moving to bimetallic clusters fabricated with atomic precision in cluster size mas well as composition.[6]

The controllability of the activity in subnanometer copper clusters and especially of selectivity when using an iron oxide support, motivated the extension of the studies of model catalysts to “real” nanoscale catalyst synthesized by wet chemistry. These catalysts were made of copper nanoparticles dispersed on iron oxide supports, and their performance will be discussed from the production of C1 to C5 products, varied by the composition of the catalysts, their morphology and reaction conditions.[7,8]

References

1. Centi, G.; Quadrelli, E. A.; Perathoner, S. Catalysis for CO_2 Conversion: A Key Technology for Rapid Introduction of Renewable Energy in the Value Chain of Chemical Industries. *Energy Environ. Sci.* **2013**, *6* (6), 1711.
2. Liu, C.; Yang, B.; Tyo, E.; Seifert, S.; DeBartolo, J.; von Issendorff, B.; Zapol, P.; Vajda, S.; Curtiss, L. A. Carbon Dioxide Conversion to Methanol over Size-Selected Cu_4 Clusters at Low Pressures. *J. Am. Chem. Soc.* **2015**, *137* (27), 8676-8679
3. Yang, B.; Liu, C.; Halder, A.; Tyo, E. C.; Martinson, A. B. F.; Seifert, S.; Zapol, P.; Curtiss, L. A.; Vajda, S. Copper Cluster Size Effect in Methanol Synthesis from CO_2. *J. Phys. Chem. C* **2017**, *121*, 10406-10412..
4. Yang, B.; Yu, X.; Halder, A.; Zhang, X.; Zhou, X.; Mannie, G. J. A.; Tyo, E. C.; Pellin, M. J.; Seifert, S.; Su, D.; Vajda, S. Dynamic Interplay between Copper tetramers and Iron Oxide Boosting CO_2 Conversion to Methanol and Hydrocarbons under Mild Conditions. *ACS Sust. Chem. Eng.* **2019**. **7**, 14435−14442.
5. Halder, A.; Lenardi, C.; Timoshenko, J.; Mravak, A.; Yang, B.; Kolipaka, L. K.; Piazzoni, C.; Seifert, S.; Bonačić-Koutecký, V.; Frenkel, A. I.; Milani, P.; Vajda, S. CO_2 Methanation on Cu-Cluster Decorated Zirconia Supports with Different Morphology: A Combined Experimental In Situ GIXANES/GISAXS, Ex Situ XPS and Theoretical DFT Study. *ACS Catal.* **2021**, *11* (10), 6210-6224.
6. Mravak, A.; Vajda, S.; Bonacic-Koutecky, V. Mechanism of Catalytic CO_2 Hydrogenation to Methane and Methanol Using a Bimetallic Cu_3Pd Cluster at a Zirconia Support. *J Phys Chem C Nanomater Interfaces* **2022**, *126* (43), 18306-18312.
7. Halder, A., Kilianová, M., Yang, B., Tyo, E.C., Seifert, S., Prucek, R., Panáček, A., Suchomel, P., Tomanec, O., Gosztola, D.J., Milde, D., Wang, H.-H., Kvítek, L., Zbořil, R., Vajda, S., Highly Efficient Cu-Decorated Iron Oxide Nanocatalyst for Low Pressure CO_2 Conversion, *Appl. Cat ,B,* **2019,** 225, 128-138 (2018)
8. Qadir, M. I., Žilková, N., Kvítek, L., Vajda, S, Atmospheric Pressure Selective Carbon Dioxide Hydrogenation to Olefin-rich Hydrocarbons by Cu/FeOx Nanoarchitectures, *in press*

Acknowledgements

S.V acknowledges the initial support by the US Department of Energy, Basic Energy Sciences, followed by funding by the European Union under Horizon Europe (project 101079142).

Challenges and performance of Cu-SCR catalysts under H2-ICE conditions

Roberta VILLAMAINA[1*], Maria Pia RUGGERI[2], Paul MILLINGTON[1], Husn ISLAM[1], Lisa ALLEN[1], David BERGEAL[2], Jill COLLIER[1]

[1]Johnson Matthey Technology Centre, Blounts Court Road, RG4 9NH, UK

[2]Johnson Matthey, Orchard Road, Royston, SG8 5H2, UK

** roberta.villamaina@matthey.com*

Significance and Relevance

This work shows the challenges which Cu-SCR will have to face if used as technology for NOx removal in H2-ICE applications. Activity testing, Operando XAS Spectroscopy and reactive characterisation were combined to collect preliminary evidence of the SCR performance and durability of state-of-the-art Cu-CHA catalyst under H2-ICE conditions, characterised by high water concentration (20-30%) and H_2 (up to 2%).

Preferred and 2nd choice for the topic: automotive and stationary emission control; sustainable and clean energy production and transport.
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster) Oral and Short oral

Introduction and Motivations

Internal combustion engines operated using H_2 as fuel (H2-ICE) will have a key role in the transition towards a zero-carbon transport society and they will expect to contribute to the global HD powertrain from 2030 onwards. Despite a history dating back to the 19th century, H2-ICEs are not yet competitive to Diesel and Gasoline engines and need to be developed. H2 ICEs will still require an after-treatment system: despite the use of a completely carbon free energy source and therefore the absence of CO and CO_2 emissions, NOx and high levels of water are still produced as by-products of the hydrogen combustion process. Due to the nature of the pollutants, Pt/Pd zeolites could be considered as a suitable solution for reducing NOx to N_2 using H_2 itself as reductant (H_2 SCR – Selective Catalytic Reduction) [1,2,]. However, it is well known the poor activity and selectivity to N_2 of these materials. NOx reduction by NH_3-SCR, combined with an ASC (Ammonia Slip Catalyst) to deal with the unconverted ammonia, could represent a better choice because of their typical outstanding performance under Diesel conditions[3]. H2-ICE conditions could be more challenging than Diesel though: this work will provide an overview on the challenges which state-of-the-art Cu-SCR catalyst will face when exposed to H2-ICE exhausts and how its SCR performance is impacted by combining activity testing, Operando Spectroscopy and reactive characterisation under relevant conditions.

Results and Discussion

H2-ICE exhausts are characterised by high water concentration (20-30%), potentially high levels of NOx (3000 ppm) and H_2 spikes (up to 2%) and S (depending on the H_2 source - i.e. grey H_2 - and from lubricant oil). The feasibility of the use of Cu-zeolite catalysts for the removal of NOx in presence of high-water and H_2 was preliminary investigated by comparing NH_3-SCR performance of a state-of-the-art Cu-CHA catalyst under Diesel conditions (7%H_2O, no H_2) and H2-ICE conditions (20% H_2O, 2%H_2). Data showed a negative impact on the NOx conversion below 250°C given by the presence of high-water concentration, with an increase in the N_2O production. However, when H_2 is added, while the activity is still affected, the selectivity improves. This effect seems to suggest an important role of H_2 on the oxidation state of Cu sites: indeed, formation of N_2O has been associated with Cu^{2+} dimers[4] and addition of H_2 could modify their population, lowering the average oxidation state of Cu sites and therefore the formation of this by-product. Dedicated Operando Spectroscopy Experiments were also performed at Diamond Light Source which confirmed an increasing fraction of Cu^{+} species on increasing H_2 concentration in the SCR base feed (Figure 1).

The durability of Cu-SCR technology in presence of higher water content, H_2 and S was also investigated. Activity data and Operando XAS data were collected on sulfated Cu catalysts under Diesel

conditions and H2-ICE conditions, showing a harsher impact of high-water content on the extent of S poisoning of Cu sites, which are less available to be involved in the SCR redox cycle with negative consequence on the SCR performance.

To summarise, preliminary data have shown that Cu-CHA are still effective catalysts for dealing with the NOx produced in H2-ICEs. However, the different environment in which Cu-CHAs are exposed could have several impacts on the SCR mechanism and the durability of these catalysts which will need to be addressed for selecting the best formulation for H2 ICE after-treatment systems.

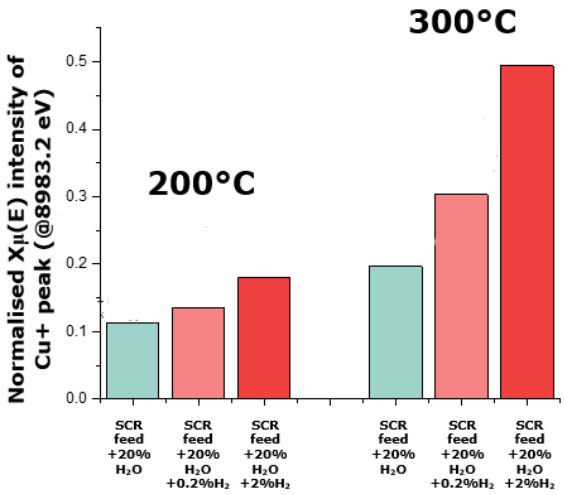


Figure 1 Normalised Xμ(E) intensity of Cu^+ peak (@ 8983.2 eV) of XAS Spectra collected during in situ experiment over a Cu-CHA catalyst at steady state conditions at 200 and 300°C. Green: SCR base feed (500 ppm NO, 500 ppm NH_3, 10% O_2) +20% H_2O; Pink: SCR base feed +20% H_2O + 0.2%H_2; Red: SCR base feed +20% H_2O + 2%H_2.

References

1. J. Shao, P. Hoang Ho, W. Di, D. Creaser, L. Olsson, *Catalysis Science & Technology* **2024**, 14(11), 3219-3234.
2. Z. Hu and R. T. Yang, *Industrial & Engineering Chemistry Research* **2019**, 58, 10140–10153.
3. I. Nova and E. Tronconi, *Fundamental and Applied Catalysis Urea-SCR Technology for deNOx After Treatment of Diesel Exhausts*, *Springer* **2014**, New York.
4. Y. Feng, T.V.W. Janssens, P.N.R. Vennestrøm, J. Jansson, M. Skoglundh, H. Grönbeck, *Journal of Physical Chemistry* **2021**, 125, 4595-4601.

Acknowledgements

This work has been externally funded by the Advanced Propulsion Centre UK (Cummins-Brunel project)

Cenosphere-based catalysts active in selected heterogeneous pro-environmental redox reactions

Paweł RYBOWICZ[1], Yana VITUSHYNSKA[1], Allison PROSZOWSKA[1,2], Tomasz POLCZYK[1], Bogdan SAMOJEDEN[3], Agata ŁAMACZ[4], Monika MOTAK[3], Marek MICHALIK[4], Andrzej ADAMSKI[*,1]

[1]*Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, 30-387 Kraków, Poland.*

[2]*Jagiellonian University, Faculty of Biology, Gronostajowa 7, 30-387 Kraków, Poland.*

[3]*AGH University of Krakow, Faculty of Energy and Fuels, Mickiewicza Ave. 30, 30-059 Kraków, Poland.*

[4]*Wroclaw University of Technology, Faculty of Chemistry, Gdanska 7/9, 50-344 Wroclaw, Poland.*

** a.adamski@uj.edu.pl*

Significance and Relevance

In accordance with main principles of the circular economy, new ways of efficient use of by-products generated in technological processes are being sought. Cenospheres, being one of the possible grain types occurring in fly ashes produced by energy sector may serve as a representative example of such by-products. As stable composite materials, cenospheres exhibit many interesting physicochemical properties, which can be exploited efficiently in a wide range of various applications including those in catalysis. This work is devoted to the use of commercial cenospheres as catalytic supports enhancing catalytic activity of copper and zinc in NO_x removal and CO_2 conversion.

Preferred and 2nd choice for the topic:
Sustainable and clean energy production and transport; Air cleaning and combustion;
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster) Oral preferred or Short Oral

Introduction and Motivations

Cenospheres are formed in high-temperature processes, accompanying energetic fossil fuel or biomass combustion (i.e. at temperatures higher than 1200°C), from non-flammable components contained in fuels. After burning the organic part, the material remaining in the combustion chamber melts and is enriched mainly in silicon, aluminum, iron and alkaline elements. In such conditions, under the influence of gases released during combustion, spherical grains of cenospheres are formed. These grains are characterized by, among others: low density and high mechanical, thermal and chemical resistance. A significant share of mullite and other aluminosilicate phases in the structure of cenospheres ensures their high thermal stability. The mentioned properties clearly suggest a high potential for using cenospheres as promising catalytic supports. Relatively low specific surface areas of cenospheres may be problematic for some applications. To overcome this disadvantage additional structural modifications are sometimes required. Our main goal was to check whether commercial cenospheres can be used as suitable support materials for transition metal oxides of catalytic interest. Another aim was to study and to elucidate the effect of cenospheres on speciation of oxometallic species stabilized on their surface.

Materials and Methods

Commercial cenospheres of various diameters (diam; expressed in μm), labelled hereafter as Cen-diam, have been impregnated with appropriate amounts of aqueous solutions of precursors, containing copper, zinc or their combinations. Impregnated samples were then calcined at 400°C or 500°C for 4 hours to obtain final catalysts. Both cenospheres and the supported/functionalized material have been structurally (XRF, XRD, RS), texturally (SEM, porosimetry) and functionally (RS, DRIFT, UV-Vis/DR) characterized in detail. Final cenosphere-based catalysts have been catalytically tested in such pro-environmental redox reactions as hydrogenation of CO_2 to methanol, dry reforming of methane and selective reduction of NO_x.

Results and Discussion

The results obtained suggested quite strong effect of cenospheres on both structure and speciation of the deposited Cu- and Zn-containing phases. Structural XRD and RS studies clearly confirmed that interactions between cenosphere surfaces and the deposited phases were rather weak, favoring the formation of CuO and ZnO three-dimensional nanorystallites even at such low concentrations of the deposited phases as 0.5 mol. % of Cu or 0.3 mol. % of Cu and 0.2 mol. % of Zn. The octahedral oxygen surrounding of Cu(II) centers was confirmed in all analyzed cases. The introduction of Zn(II) dopants does not significantly affect the speciation of oxo-copper species, causing only slight distortion of the Cu(II) oxygen environment. As it was suggested by SEM/EDX analysis, distribution of the deposited phases on cenosphere surfaces was non uniform (cf. Fig. below). Simultaneously, as revealed by DRIFT, due to relatively many different stabilization sites, heterogeneity of hydroxyls stabilized on the surface of cenosphere-supported catalysts was distinctly strong. These effects have quite pronounced catalytic consequences. It is noteworthy that not only the initial composition of the investigated cenosphere-based samples, but also their calcination temperature, played the key role for both surface architecture and electronic properties. Additionally, our studies confirmed, that cenosphere-supported oxide phases were thermally stable and they can be considered as useful catalytic materials, even for such demanding reactions like e.g. high-temperature dry reforming of methane. Similar stability has been observed for cenosphere-based catalysts tested in hydrogenation of CO_2 to methanol. The use of cenospheres from fly ashes produced by energy sector to obtain valuable catalytic materials is a very good example of circular economy.

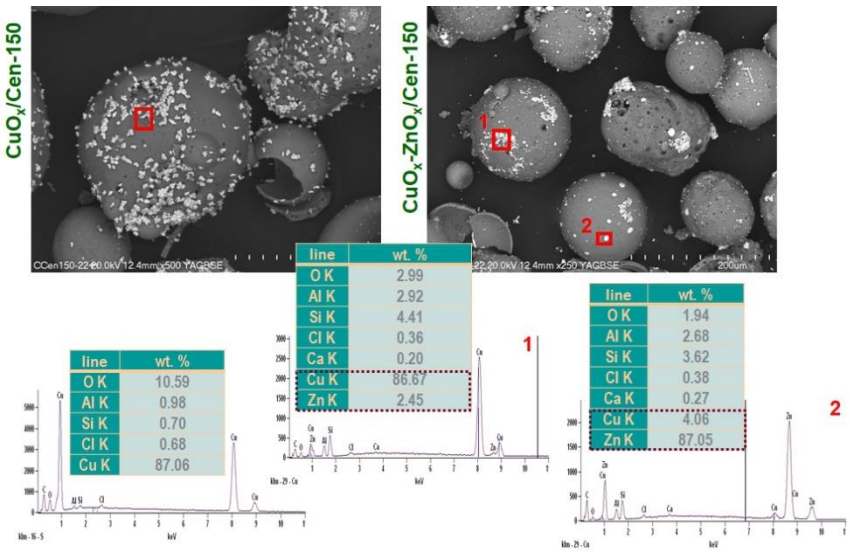


Figure. SEM images of the selected cenosphere-supported samples and the corresponding results of their EDX analysis.

Acknowledgements

The research has been supported by a grant from the Priority Research Area Anthropocene (FP Man-Mind-Environment Hub) under the Strategic Programme Excellence Initiative at the Jagiellonian University. Contribution of P.R. to this work was also supported in the framework of POWR.03.02.00-00I004/16 and of Talent Management POB Anthropocene grants.

Catalytic ozonation of pharmaceuticals – From experiments to modelling

Soudabeh SAIED[1,2], Pasi TOLVANEN[1], Vincenzo RUSSO[1,3], Pasi TOLVANEN[1], Tapio SALMI*[1,3]
[1]*Åbo Akademi, Laboratory of Industrial Chemistry and Reaction Engineering (TKR), FI-20500 Turku/Åbo, Finland*
[2]*Linde + Robinson Laboratories, California Institute of Technology, Pasadena 91125, United States*
[3]*Università di Napoli 'Federico II', Chemical Sciences, IT-80125 Napoli, Italy*
**tapio.salmi@abo.fi*

Significance and Relevance

A new kinetic model based on molecular mechanisms was developed for the destruction of pharmaceuticals by combined ozonation and heterogeneous catalysis. The model describes the concentration courses of ibuprofen and its partially oxidized products and can be applied to other pharmaceuticals. Valuable insights into the design and optimization of catalytic ozonation processes were obtained, thus enabling an improved treatment efficiency and minimized environmental impact.

Preferred and 2nd choice for the topic: Water treatment; Multiscale modelling
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster) Oral

Introduction and Motivations

Hundreds of pharmaceuticals enter aquatic systems via several pathways: incomplete metabolism and subsequent excretion of medications through human excreta, agricultural runoff containing antibiotics and other veterinary drugs used in animal husbandry, and industrial discharges. The surface and ground waters get polluted by these contaminants. Existing commercial technologies are unable to eliminate all the pharmaceuticals from wastewaters and in the worst case, only partial oxidation of the pharmaceuticals takes place leading to harmful or even poisonous intermediates[1,2]. Ozonation is an appropriate water cleaning technology but ozonation alone is not always sufficient to achieve efficient total oxidation of the organic species. Combination of ozonation with heterogeneous catalysis is an efficient method for the degradation of pharmaceuticals and it was studied in detail in this work.

Materials and Methods

Experimental kinetic data were obtained with a laboratory-scale semi-batch reactor by varying the key operational parameters: temperature, gas flow rate and stirring arrangement. The catalyst (Cu-H-Beta-150DP) was placed in a rotating bed. An ozone generator was connected to the reactor vessel via a dispenser. Liquid-phase samples were withdrawn and analyzed with GC, LC-MC and NMR[1].

Results and Discussion

This study presents a new and comprehensive mathematical model describing the degradation of ibuprofen (IBU) and its transformation by-products in aqueous environment utilizing both ozonation and heterogeneously catalyzed ozonation as a semi-batch process. The model incorporates the formation and subsequent degradation of four partially oxidized by-products: 2-OH-IBU, 1-OH-IBU, 1-OXO-IBU, and APMP. The reaction paths are displayed in Figure 1.

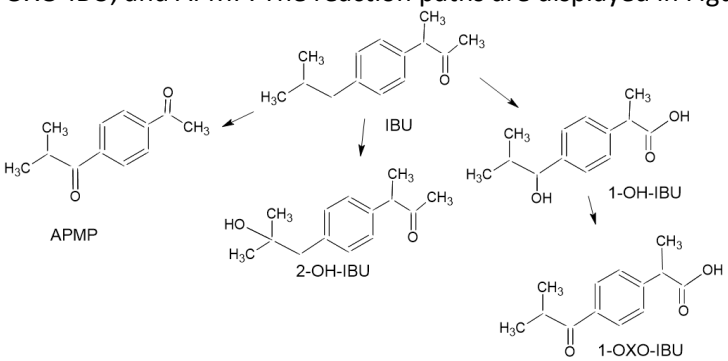


Figure 1. Partially oxidized intermediates of IBU. The intermediates were confirmed by NMR and MS[1].

The reaction mechanism is very complex since it comprises both non-catalytic and catalytic steps. Elementary reaction steps for the degradation of IBU as well as formation and disappearance of the by-products were assumed and rate equations were derived based on the elementary steps and quasi-steady state hypothesis for the radical intermediates. The reaction steps are summarized below.

$$O_3 + H_2O \rightarrow 2HO^\circ + O_2 \qquad O_3 + HO^\circ \xrightarrow{k_1} O_2 + HO_2^\circ \qquad O_3 + HO_2^\circ \xrightarrow{k_2} 2O_2 + HO^\circ \qquad 2HO_2^\circ \xrightarrow{k_T} 2O_2 + H_2O_2$$

$$IBU + OH^\circ \overset{K_{c1}}{\rightleftharpoons} 2-OH-IBU + H^\circ \qquad IBU + OH^\circ \overset{K_{c2}}{\rightleftharpoons} 1-OH-IBU + H^\circ$$

$$1-OH-IBU \overset{K_{c3}}{\rightleftharpoons} 1-OX-IBU + H_2 \qquad IBU \overset{K_{c4}}{\rightleftharpoons} APMP \qquad H^\circ + OH^\circ \rightarrow H_2O$$

Besides the kinetics, the gas-liquid mass transfer parameters and experimentally measured gas solubilities were included in the mathematical model. The mass balances, the ordinary differential equations were solved using MATLAB. The kinetic parameters were estimated with non-linear regression analysis. The model predicts accurately the concentrations of IBU and the by-products over time; an example of the model fit to experimental data is shown in Figure 2. This model offers valuable insights into the design and optimization of ozonation processes for the IBU removal from wastewaters, thus enabling an improved treatment efficiency and minimized environmental impact. The concept applied in this work can be expanded to other pharmaceutical molecules.

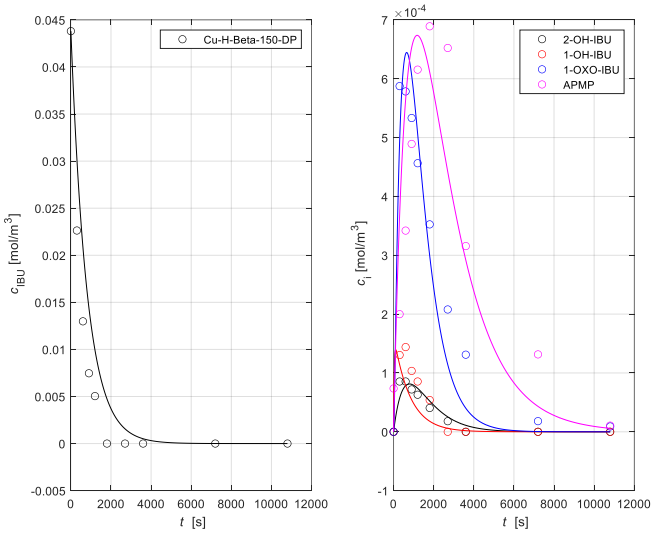


Figure 2. Catalytic ozonation of IBU in the presence of Cu-H-Beta-150-DP and concentrations of by-products formed during the IBU decomposition. Experimental data: symbols, model predictions: continuous lines.

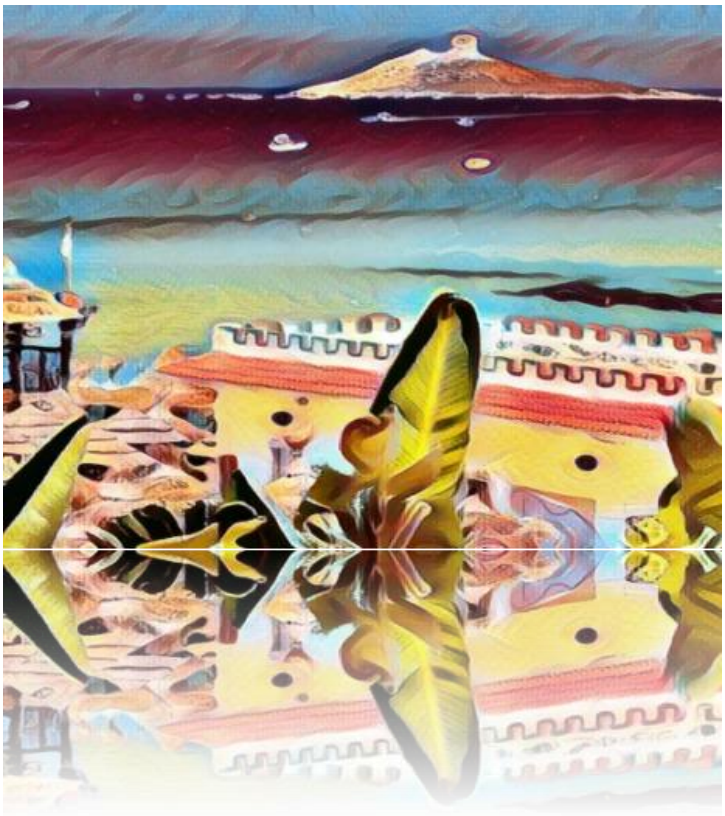
References

1 M. Kråkström, S. Saeid, P. Tolvanen, N. Kumar, T. Salmi, L. Kronberg, P. Eklund, *Ozone: Science & Engineering* **2021**, 44, 1–15.
2 S. Saeid, P. Tolvanen, N. Kumar, K. Eränen, J. Peltonen, M. Peurla, J.P. Mikkola, A. Franz, T. Salmi, *Applied Catalysis B Environmental* **2018**, 230 77–90

Acknowledgements

The work is a part of the activities of Johan Gadolin Process Chemistry Centre (PCC) at Åbo Akademi. Financial support from Åbo Akademi is gratefully acknowledged (Soudabeh Saeid).

ORAL ABSTRACTS



Natural Gas Vehicle post-combustion catalysts : How to manage support effect to magnify the performances of noble metals in methane abatement

Amaury Decoster, Fabien Dhainaut, Pascal Granger*,[1]

[1]*Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, F-59000 Lille, France*

Significance and Relevance

Nowadays, catalytic end-of-pipe technologies are widespread worldwide. However, important challenges are coming across associated to the transition from liquid fueled engines to gas fueled engines. In the frame of this transition, natural gas can be attractive in terms of carbon footprint and less harmful atmospheric pollutant emissions. Existing catalytic technologies use palladium extensively to remove traces of methane in the exhaust acting as powerful greenhouse gas. The European community classified PGMs as strategically important materials stimulating a strong reduction in their uses. Stabilization/magnification of PGM efficiency thanks to support effect with the use of spinel structure has been evaluated. Better insights into reaction mechanisms driven by the extent of the Pd-support interface can provide useful guidelines to comply with these requirements.

Preferred and 2nd choice for the topic: Automotive and stationary emission control and Fundamental advances in understanding catalysis as second choice
Preferred presentation: (Oral preferred or Short Oral)

Introduction and Motivations

Nowadays, end-of-pipe catalytic technologies are widespread worldwide. However important challenges are coming across associated to the transition from liquid powered engines to gas powered engines which should lead to further technical adaptations to improve the efficiency of the existing catalytic end-of-pipe technologies.[1] In the frame of this transition, natural gas can be considered much more attractive than diesel and gasoline fueled-engines in terms of reduction of atmospheric pollutant emissions as well as economic terms .[2,3] Presently catalytic after-treatment technologies are intimately related to an extensive use of platinum group metal (PGM) as well as rare earths which have been classified by the European community as strategically important materials for which a reduction in the use is strongly advised. On this basis, new conceptual ideas should emerge that guide innovation in the development of new generations of post-combustion catalysts. Possible alternatives integrating reduction in the use of PGM should obey to specific prerequisites such as : *(i)* the promotion of the dispersion of PGM avoiding strong inhibition effects and structural instabilities *(ii)* the magnification of their intrinsic catalytic properties.

Spinel structures have been developed $Co_xFe_{4-x}O_4$ further doped with palladium. Their intrinsic catalytic properties are related to the oxidation state of cobalt and the reactivity of lattice oxygen species depending on the Co-O bond strength.[4,5] Both appear as key parameters to activate the C-H bond breaking in CH_4 molecule. Palladium is regarded as a benchmark for methane combustion exceptionally in lean conditions corresponding to the stabilization of PdO. On the other hand, investigations of catalytic performances at high temperature in an oxygen-depleted environment are scarce while important challenges lie in the destabilization of Pd-O leading to unreactive metallic Pd species.[6] Particular attention was paid to the protocol used for Pd incorporation, *i.e.* one pot vs. sequential method that lead to different degree of dispersion and interface. Catalytic performances for the CH_4/O_2 reaction were evaluated at various richness in the presence and in the absence of water. Thermal aging has been investigated showing that the thermal stability is intimately related to the selected method for Pd incorporation governing the Pd-support interface driving the kinetics of this reaction.

Results and Discussion

In a first attempt, different cobalt compositions in $Co_xFe_{3-x}O_4$ mixed oxides were examined showing magnified intrinsic catalytic properties for $CoFe_2O_4$ pre-reduced in H_2 at 250°C. Pre-reductive treatment showed a complete reduction of Co^{3+} into Co^{2+} while Fe^{3+} valency remains unchanged. Palladium was incorporated by impregnation on calcined samples or during the coprecipitation step according to a *one pot* method corresponding $Pd/CoFe_2O_4$ or $Pd\text{-}CoFe_2O_4$ catalysts respectively. Both were similarly pre-reduced at 250°C before reaction. XRD analysis in Fig .1 reveals a spinodal decomposition process resulting in the coexistence of two spinel structures which differ from their composition. TEM-EDS analysis confirm the presence of Co- and Fe-rich spinel structures. Raman and Mössbauer spectroscopy analyses also show different distributions of Fe^{3+} cations in tetrahedral and octahedral symmetry.

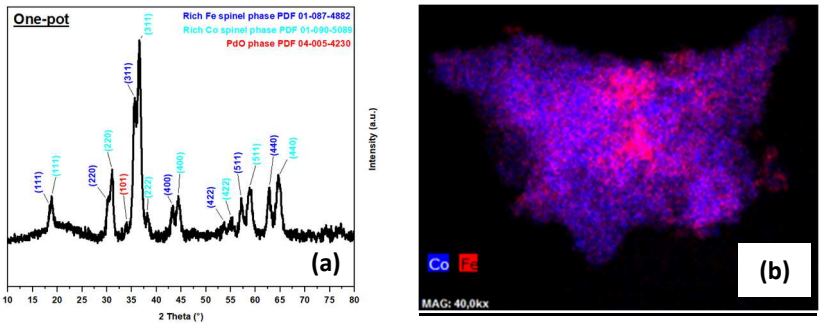


Figure 1. XRD patterns recorded on one pot $Pd\text{-}Co_2FeO_4$ (a); TEM-EDS analysis recorded on Co_2FeO_4 calcined at 600°C in air (b).

In situ XPS study, carried out on Co_2FeO_4 and doped-Pd Co_2FeO_4 catalysts showed the evolution of the oxidation state of Pd and transition metals after reduction at moderate temperature, *i.e.* 250°C. *In situ* reduction of undoped- Co_2FeO_4 only involves the reduction of Co^{3+} into Co^{2+}. On the other hand, Pd incorporation promotes the reduction of Co^{3+} and Fe^{3+} up to the formation of metallic Co^0 and Fe^0 species. It appears that these changes are weakly sensitive to the method use for Pd incorporation.

The kinetics has been investigated in stoichiometric and lean conditions corresponding to O_2/CH_4 ratio of respectively 2 and 20. Reaction rate measurements were discussed and modelled according to two reaction mechanisms involving reactive chemisorbed O_* species from the dissociative adsorption on palladium or reactive surface lattice 'O' species from the spinel. Both have been equally considered and their contribution has been estimated based on the adjusted kinetic and thermodynamic constants for adsorption. In fact, the richness plays a determining role with the prevalence of surface lattice 'O' species in oxygen depleted environment. Aging leads to controversial observations as for one-pot samples the involvement of surface lattice 'O' species accentuates irrespective of the richness conditions while the reverse tendency affect impregnated samples becoming after aging more sensitive to the reactivity of chemisorbed O_* species on Pd reflecting a deterioration of the Pd-support interface.

References

1. Y. Zheng, A. Decoster, V. Parvulescu, P. Granger, *Catal. Sci. Technol.* **2024***, 14,* 4106.
2. L.G. Andersson, *Renewable Sustainable Energy Rev.* **2015**, *47*, 162.
3. M.I. Khan, T. Yasmin, A. Shakoor, *Renewable Sustainable Energy Rev.* **2015**, *51*, 785.
4. J. Li, H. Yuan, G. Li, J. Jeng, *J. Magn. Magn. Mater.,* **2010***, 322(21),* 3396.
5. Neha, R. Prasad, S. Vir Singh, *J. Environ. Chem. Eng.*, **2020***, 8,* 103627.

NH_3-SCR over Cu-CHA from first principles

Henrik Grönbeck*,[1]
[1]*Competence Centre for Catalysis and Department of Physics, Chalmers University of Technology, Göteborg, Sweden*
**ghj@chalmers.se*

Significance and Relevance

The results provide atomic-level understanding of the hierarchy of effects that determine the NH_3-SCR activity over Cu-exchanged chabazite catalysts at low- and high-temperatures. The low-temperature activity is determined by pairing of mobile $Cu(NH_3)_2^+$ complexes and blocking of the active sites by NH_3, whereas the high-temperature activity is limited by NH_3-blocking of single framework-bound Cu species. The first-principles based kinetic model describes accurately the non-monotonic temperature dependence of the activity.

Introduction and Motivations

NO_x emission control continues to be a major challenge in lean-burn engine exhaust after treatment due to increasingly stricter legislations. The leading technology for NOx reduction to N_2 and H_2O in oxygen excess is selective catalytic reduction using ammonia as the reducing agent (NH_3-SCR). A state-of-the-art catalyst for NH_3-SCR is chabazite zeolite functionalized with Cu (Cu-CHA). Cu-CHA has high activity and selectivity for NH_3-SCR over a wide temperature range and is, moreover, hydrothermally stable at high temperatures.

The conversion of NOx over Cu-CHA under standard SCR conditions shows a nonmonotonic trend with respect to temperature, with a minimum at about 350 °C. This minimum results in the, so-called, "seagull" profile and indicates that different reaction mechanisms dominate at low and high temperatures. An additional indication that the reaction mechanism changes with temperature is different initial exponential increases of the conversion in the low- and high-temperature regimes. The temperature dependence of the nonselective N_2O formation during the NH_3-SCR is yet another indication that the NH_3-SCR reaction follows different mechanisms at low and high temperatures.

Understanding the dominating reaction mechanisms for NH_3-SCR over Cu-CHA provides a handle to further improve the performance.

Materials and Methods

First-Principles Calculations. Spin-polarized DFT calculations are performed with the Vienna Ab-initio simulation package. The gradient-corrected Perdew–Burke–Ernzerhof functional, augmented with a Hubbard-U term and van der Waals corrections, is used to describe exchange–correlation effects. Mean-field microkinetic modeling and kinetic Monte Carlo simulations are used to explore the consequences of the first-principles reaction landscapes and facilitate comparison to experiments.

Results and Discussion

Figure 1 shows the proposed reaction cycle at low and high temperatures. The low temperature mechanisms proceeds over a pair of mobile $Cu(NH_3)_2^+$ complexes. The reaction can proceed only when two $Cu(NH_3)_2^+$ complexes are in the same CHA-cage. O_2 adsorbs over the two complexes forming a peroxo-complex, $[Cu_2(NH_3)_4O_2]^{2+}$. NO and NH_3 couple over the peroxo-complex forming the intermediates H_2NNO and HONO, which diffuse to Bronsted acid sites where they decompose into N_2 and H_2O with low barriers [1]. H_2NNO has been suggested to decompose also over a $[Cu_2(NH_3)_4OOH]^{2+}$ complex generating N_2O and H_2O [2]. The reaction can be hindered by NH_3 adsorption onto the Cu-cations when being in a Cu(II) oxidation state. The kinetic analysis [3] shows that the NH_3-blocking determines the light-off temperature. Taking the pairing of $Cu(NH_3)_2^+$ complexes into account by kinetic Monte-Carlo simulations [4] shows that the turn-over frequency is determined by the stability

of the paired $Cu(NH_3)_2^+$ complexes together with the relative stability of NO and NH_3 adsorption onto the peroxo-complex.

The low- and high-temperature mechanisms are linked via the decomposition of the $Cu(NH_3)_2^+$ complexes forming framework-bound $CuNH_3^+$ species [5]. The desorption of NH_3 forming framework bound Cu^+ is found to be limiting the high-temperature mechanism. The non-monotonic NO-conversion profile is, thus, found to originate from i) the low coverage of the peroxo-complex and ii) NH_3-blocking of the high-temperature mechanism.

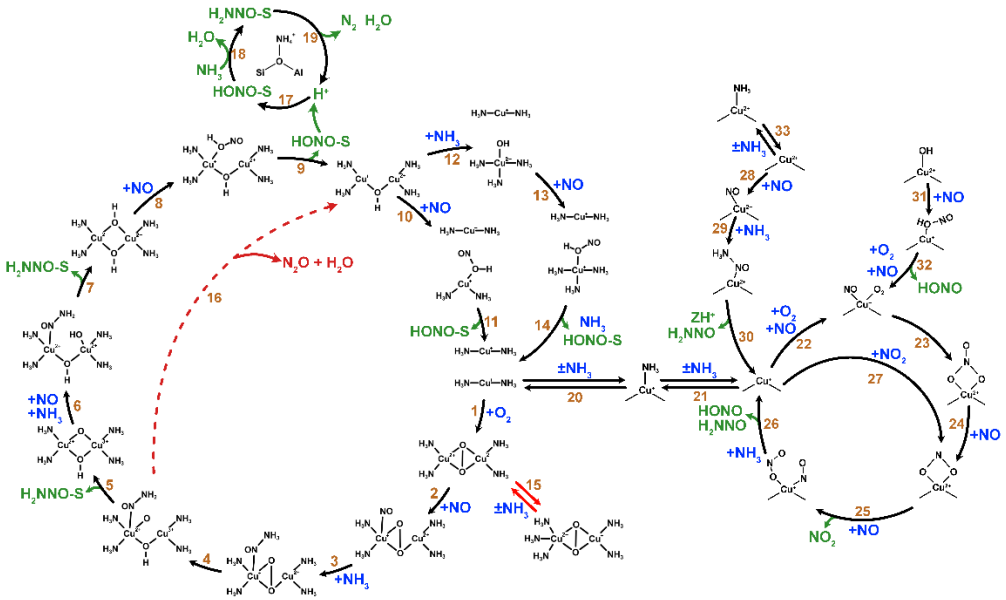


Figure 1. The proposed DFT-based reaction paths at low (left) and high (right) temperatures.

References

1. L. Chen, T.V.W. Janssens, P.N.R. Vennestrøm, J. Jansson, M. Skoglundh, H. Grönbeck, *ACS Catalysis* **2020**, *10*, 5646.
2. Y. Feng, T.V.W. Janssens, P.N.R. Vennestrøm, J. Jansson, M. Skoglundh, H. Grönbeck, *J. Phys. Chem. C* **2021**, *125*, 4595.
3. Y. Feng, X. Wang, T.V.W. Janssens, P.N.R. Vennestrøm, J. Jansson, M. Skoglundh, H. Grönbeck *ACS Catalysis* **2021**, *11*, 14395.
4. Y. Feng and H. Grönbeck, *ChemPhysChem* **2024**, *25*, e202400558.
5. Y. Feng, T.V.W. Janssens, P.N.R. Vennestrøm, J. Jansson, M. Skoglundh, H. Grönbeck, *J. Phys. Chem. C* **2024**, *128*, 6689.

Acknowledgements

Financial support from the Swedish Energy Agency (47110-1). The Competence Centre for Catalysis (KCK) is hosted by Chalmers University of Technology and financially supported by the Swedish Energy Agency (52689-1) and the member companies Johnson Matthey, Perstorp, Powercell, Preem, Scania CV, Umicore and Volvo Group. The calculations were performed at PDC (Stockholm) through a NAISS grant.

Oxidative half-cycle of SCR NO_x on single and dual copper sites of CuSSZ-13 catalyst via NO_2, nitrates and nitrites formation – spectroscopic and thermodynamic DFT background for reaction networks

Bartosz MOZGAWA,[1] Filip ZASADA,[1] Monika FEDYNA,[1] Kinga GÓRA-MAREK,[1] Zbigniew SOJKA,[1] Piotr PIETRZYK*,[1]
[1]*Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, Krakow, Poland.*
** piotr.pietrzyk@uj.edu.pl*

Significance and Relevance

The mechanistic pathways of Cu redox changes in SSZ-13 zeolite during NO SCR were investigated based on the evolution of the selective NO oxidation cycle. Combined use of *ab initio* thermodynamics (DFT model), spectroscopy (EPR, IR), and catalytic tests (temperature-programmed using isotopically labeled $^{18}O_2$) revealed three principal routes of NO_2 production. Direct NO reaction with O_2 includes the HONO pathway, the metal-redox pathway, and the ligand-redox pathway. They involve the comproportionation of surface nitrate adducts with NO, and versatile HONO behavior as a key factor.

Preferred and 2nd choice for the topic: Automotive and stationary emission control, Fundamental advances in understanding catalysis
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

NH_3-SCR is generally factored into the reduction half-cycle (RHC) with the participation of NH_3 and NO, and the oxidation half-cycle (OHC), where NO and O_2 are involved.[1,2] The mechanism of RHC has been addressed in several articles, and a consensus has been achieved about its main features.[3] The OHC stage is examined less intensively, and its mechanism at medium and high temperatures is still debated.[4] In this contribution, we aimed to provide a thermodynamic feasibility study for interpreting the complex network of the NO selective catalytic oxidation (NO-SCO) reactions by unraveling meaningful pathways of NO_x generation, its reactivity, and evolution under NO oxidation conditions.

Materials

Two types of CuSSZ-13 zeolites that differ in the Si/Al ratio, the Al sites' distribution, and the copper loading method were examined. The sample prepared by impregnation of NH_4SSZ-13 with a solution of $CuCl_2$ is labeled i-CuSSZ-13 (Si/Al = 7.9 with 70% of the Al atoms as singles, total Cu content 780 μmol/g), and that prepared by one-pot synthesis as o-CuSSZ-13 (Si/Al = 3.4, total Cu content 590 μmol/g). Detailed descriptions of the synthesis protocols and characterization results of these samples have been provided in our previous articles,[5,6] including quantification of all types of active sites of copper: Cu^{2+} (330 and 140 μmol/g), Cu^{2+}-OH^- (30 and 255 μmol/g), and Cu^{2+}-O^{2-}-Cu^{2+} (220 μmol/g and undetermined amount) for o-CuSSZ-13 and i-CuSSZ-13, respectively. The latter sample contained 325 μmol/g nano-CuO/Cu-oxo species in total, while the concentration of Brønsted sites was equal to 600 μmol/g (o-CuSSZ-13) and 160 μmol/g (i-CuSSZ-13). Furthermore, from analysis of the EPR parameters of divalent copper in o-CuSSZ-13, 80% occupies 6MR, whereas 20% - 8MR sites. In the case of o-CuSSZ-13, the occupancies are equal to 54 and 46 %, respectively.

Results and Discussion

Molecular DFT modeling coupled with first principles thermodynamic (FPT), spectroscopic (EPR/IR), and catalytic investigations into a complex network of reactions involved in the interaction of NO and O_2 with a comprehensive variety of active centers (Cu^{2+}, Cu^+, Cu^{2+}-OH^-, Cu^{2+}-O^{2-}-Cu^{2+}, Cu^{2+}-O_2^{2-}-Cu^{2+} and segregated CuO) of the CuSSZ-13 zeolites were carried out. The structure, electronic, and magnetic properties of various adducts with the reactants were ascertained with DFT calculations. In contrast, their thermal stability and reactivity were assessed using the 2D thermodynamic diagrams, $\Delta G(p,T)$, constructed for a wide range of experimental conditions. The course of selective catalytic oxidation of NO (NO-SCO) with $^{16}O_2$ or $^{18}O_2$ was examined by temperature-programmed surface reaction (TPSR),

using two types of CuSSZ-13 catalysts of controlled copper speciation. Corroborative IR and EPR measurements revealed multiple molecular pathways of NO and O_2 interaction with the single (Cu^{2+}, Cu^{+}, Cu^{2+}-OH^{-}), and dual (Cu^{2+}-O^{2-}-Cu^{2+}, Cu^{2+}-O_2^{2-}-Cu^{2+}) copper centers of the 6MR and 8MR topology, and with segregated CuO. The progress of the investigated reactions was evaluated using the calculated FPT thermodynamic profiles. The temperature behavior and reactivity of the critical intermediates (NO, HONO, nitrate, and nitrite) and their dynamic transformations into NO_2 were elucidated. The established complex reaction network was successfully used to clarify the temperature dependence of the experimental NO-SCO profiles, also providing a mechanistic background for interpreting the nature of the oxidative half-cycle of the selective catalytic reduction of NO over Cu-SSZ-13 catalysts. The unraveled redox reactions were classified into metal (cationic) redox, ligand (anionic) redox, and HONO redox cycles, where comproportionation of surface nitrate adducts with NO plays a crucial role. The Cu^{2+}-OH^{-} species were identified as versatile active centers for NO_2 formation via the HONO pathway. Elusive HONO intermediates allow for chemical communication between the individual redox cycles. Depending on the actual reaction conditions, HONO can act as a reduction agent for Cu^{2+} with the electroprotic formation of NO_2, a source of nitrites upon deprotonation, or as an oxidant of Cu^{+} with the formation of H_2O and NO. The significant difference in the Cu^{2+} cations' reactivity in the 6MR and 8MR rings is apparent at the metal redox pathway, where Cu^{2+}/6MR are spectators and Cu^{2+}/8MR are active species. Dimeric copper centers with the bridging oxo and peroxo moieties can produce a variety of nitrates and nitrites via ligand redox mechanisms. In addition, we found that segregated CuO nanocrystals contributed to NO oxidation only at high temperatures (T > 400 °C), leading to the isotopic scrambling of ^{18}O-labeled oxygen and nitric oxide.

The obtained results allowed us to establish a comprehensive network of reactions involved in the NO oxidation and the temperature windows of their occurrence. We provided an interpretation of temperature-programmed desorption and surface reaction profiles of NO oxidation based on copper speciation within CuSSZ-13 zeolite (Figure 1).

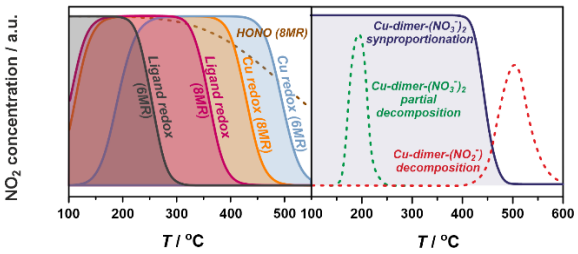


Figure 1 Thermodynamic range of the investigated NO_2 formation pathways on mononuclear copper centers in 8MR and 6MR sites (left-hand side panel). Temperature-programmed NO_2 formation reaction profiles for dimeric copper centers (right-hand side panel).

References

1. C. Paolucci, A.A, Verma, S.A. Bates, V.F. Kispersky, J.T. Miller, R. Gounder, W.N. Delgass, F.H. Ribeiro, W.F. Schneider, *Angew. Chem. Int. Ed.* **2014**, *53*, 11828.
2. T.V.W. Janssens, H. Falsig, L.F. Lundegaard, P.N.R. Vennestrom, S.B. Rasmussen, P.G. Moses, F. Giordanino, E. Borfecchia, K.A. Lomachenko, C. Lamberti, S. Bordiga, A. Godiksen, S. Mossin, P.A. Beato, *ACS Catal.* **2015**, *5*, 2832.
3. W. Hu, F. Gramigni, N.D. Nasello, N. Usberti, U. Iacobone, S. Liu, I. Nova, X. Gao, E. Tronconi, *ACS Catal.* **2022**, *12*, 5263.
4. R. Daya, D. Trandal, U. Menon, D.J. Deka, W.P. Partridge, S.Y. Joshi, *ACS Catal.* **2022**, *12*, 6418.
5. M. Fedyna, B. Mozgawa, F. Zasada, K. Góra-Marek, J. Gryboś, W. Piskorz, C. Yin, Z. Zhao, P. Pietrzyk, Z. Sojka, *Appl. Catal. B: Environ.* **2023**, *325*, 122309.
6. B. Mozgawa, F. Zasada, M. Fedyna, K. Góra-Marek, E. Tabor, K. Mlekodaj, J. Dědeček, Z. Zhao, P. Pietrzyk, Z. Sojka, *Chem. Eur. J.* **2021**, *27*, 17159.

Ternary Me–P–Si oxides for catalytic conversion of biomass-derived chemicals: a closer look at the surface.

Elisabetta FINOCCHIO*, Antonella GERVASINI, Sebastiano CAMPISI, Aurelio BIFULCO, Claudio IMPARATO, Antonio ARONNE.

[1] *Università di Genova, Dip. Ingegneria Civile, Chimica e Ambientale, Via Opera Pia 15, Genova, Italy.*

[2] *Università di Milano, Dip. Chimica, Via Camillo Golgi 19, Milano, Italy.*

[3] *Università di Napoli Federico II, Dip. Ingegneria Chimica, dei Materiali e della Produzione Industriale, P.le Tecchio 80, Napoli, Italy.*

* *Elisabetta.Finocchio@unige.it*

Significance and Relevance

Silica based ternary catalysts with phosphorus and niobium, titanium or zirconium dispersed in the network have been prepared through an innovative one-pot sol-gel process. Their modulated acidity, due to different exposed surface sites, makes these materials promising candidates for heterogeneous catalysis in conversion of chemicals from biomasses, such as alcohols, ethers, saccharides. A systematic investigation of the surface properties of ternary Me–P–Si (Me = Nb, Ti, Zr) is here presented.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion, Fundamental advances in understanding catalysis.
Preferred presentation: Oral preferred or Short Oral.

Introduction and Motivations.

Me-P_2O_5-SiO_2 mixed oxides are active solid catalysts for conversion of biomass-derived chemicals, whose surfaces show a complex distribution of active and adsorption sites depending on the support, the support modifications and the chemical nature of the metals. The tunable distribution of exposed Brønsted and Lewis acidic sites leads to catalysts that can coordinate and activate n-type bases, such as oxygenates compounds (alcohols, ethers, saccharides). The introduction of transition metals in a ternary oxide may deeply modify the distribution and strength of acid sites and thus the catalytic performances. In a previous work, Nb-P-Si catalysts has been synthesized by sol-gel route and tested in different reactions, such as ethanol dehydration and diethylether conversion. Results were encouraging in view of applications in industrial chemistry[1,2,3]. Very recently, we undertook an extensive investigation of surface properties of Ti-P-Si and Zr-P-Si ternary systems, synthetized by a one-pot hydrolytic sol-gel route, to be compared to the previous reference formulation Nb-P-Si. The alternative approach adopted in the synthesis of Ti-P-Si and Zr-P-Si ternary materials, with respect to the traditional ones, such as grafting or impregnation, has allowed to obtain the formation of a homogeneous dispersion of the active phase into the siloxane matrix[4]. In this work a thorough investigation on the nature and the amount of exposed acidic sites together with catalytic data on sucrose conversion, as test reaction, are reported. The issue of the stability of the catalysts in demanding conditions is also addressed.

Materials and Methods.

The ternary oxides were synthesized by the hydrolytic sol-gel route described in detail in refs. 3 and 4, using H_3PO_4 as P precursor, ammonium niobium oxalate as Nb precursor and alkoxides as Zr, Ti and Si precursors, keeping Me/P atom ratio equal to 2. Nominal molar compositions of MePSi materials considered here are: $5Nb_2O_5{\cdot}2.5P_2O_5{\cdot}92.5SiO_2$ (NbPSi), $10TiO_2{\cdot}2.5P_2O_5{\cdot}87.5SiO_2$ (TiPSi) and $10ZrO_2{\cdot}2.5P_2O_5{\cdot}87.5SiO_2$ (ZrPSi). One binary P_2O_5-SiO_2 (PSi) sample, as well as the pure support silica, were also synthesized as reference. The resulting materials have been characterized by TGA, XRD, BET. Acid site number was quantified by gas-solid titrations by NH_3 probe adsorption in flowing dynamic experiments and by pyridine probe molecule adsorption in situ FT IR studies, both on dry and on hydrated surfaces. Residual acidity was also evaluated by probe molecules adsorption over samples submitted to water pretreatment.

Results and Discussion

The surface chemistry of silica materials is driven by the exposed silanol groups, which show a weak protonic acidity. The modification with phosphorus and niobium leads to the appearance of Brønsted acid sites[3], while Me addition also introduces a medium-weak Lewis acidity, associated to the presence of exposed coordinatively unsaturated Zr and Ti ions. Likely, the presence of electron-withdrawing atoms also affects acidity of the nearby silanol groups. Over the fully hydroxylated surface the same type of sites, that is weak and Brønsted protonic sites and Lewis sites is detected, the latter at a slightly lower extent (Figure 1,a and b). Possibly, Lewis sites are more evident in the spectrum of ZrPSi sample, in agreement with XPS results pointing out a relative enrichment of this metal sites at the catalyst surface[4]. N_2 adsorption-desorption isotherms reveal the microporous nature of MePSi samples. Comparing the effect of Ti and Zr modifications, slightly higher surface area values for TiPSi (395 ± 11 m^2/g) than ZrPSi (346 ± 37 $m^2\ g^{-1}$) were reported, while the two samples show similar pore volumes (ca. 0.2 $cm^3\ g^{-1}$) and pore size distributions dominated by small micropores. The total number of acid sites was titrated using ammonia as a basic probe molecule: TiPSi and ZrPSi showed similar acid character with similar acid site density (about 1.7 $\mu eq\ m^{-2}$)[4].

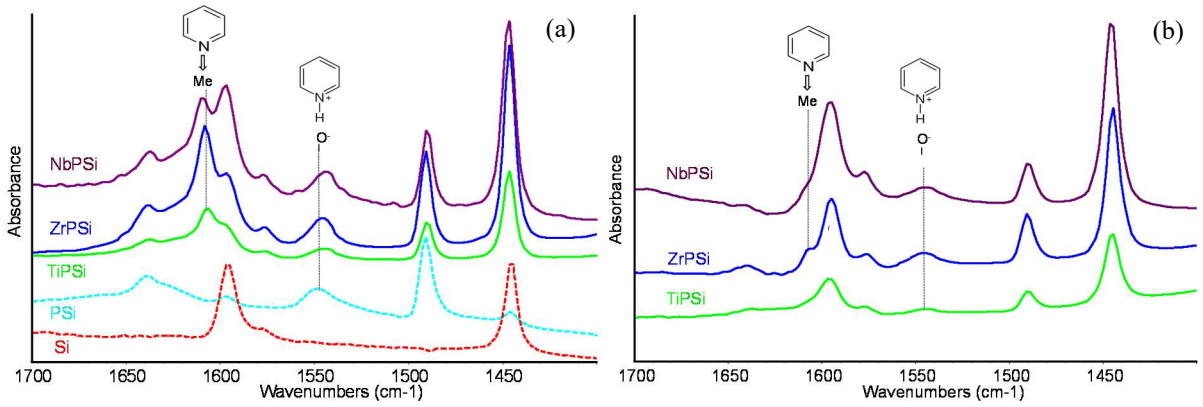


Figure 1. FT IR subtraction spectra of pyridine adsorbed and desorbed at 150 °C over Nb, Ti, Zr ternary systems: (a) partially dehydroxylated surface, (b) highly hydroxylated surface. The spectrum of the corresponding activated surface has been subtracted.

It is possible to suggest that the acid character of the surfaces is mainly ascribable to surface hydroxy groups, either Si–OH (whose acidity might be enhanced by nearby metal ions), and P–OH groups, in agreement with FTIR data of adsorbed pyridine[4]. Preliminary catalytic data on the hydrolysis of sucrose confirmed the activity of Zr and Ti based catalysts, also indicating a faster reaction rate over the Ti-P-Si ternary oxide. Surface studies are now in progress on the modification of these catalysts eventually occurring after pretreatments in harsh conditions.

References

1. A.Gervasini, S. Campisi, P. Carniti, M.Fantauzzi, C. Imparato, N.J. Clayden, A. Aronne, A.Rossi, *Applied Catalysis A General* **2019**, *579*, 9.
2. N.J. Clayden, C. Imparato, R. Avolio, G. Ferraro, M.E. Errico, A. Vergara, G. Busca, A. Gervasini, A. Aronne, B. Silvestri, *Green Chemistry* **2020**, *22*, 7140.
3. G. Garbarino, G.Pampararo, E. Finocchio, G.Busca, A. Gervasini, S. Campisi, B. Silvestri, C. Imparato, A. Aronne, *Microporous Mesoporous Materials* **2022**, *343*, 112190.
4. C. Imparato, E. Finocchio, S. Campisi, M.Bigica, A. Gervasini, A.Bifulco, R.Avolio, N.J.Clayden, M.E.Errico, A. Aronne, *Materials Today Chemistry*, **2024**, *38*, 102126.

Iron-catalyzed cooperative red-ox mechanism for the simultaneous conversion of nitrous oxide and nitric oxide

Filippo BUTTIGNOL[1,2], Jörg W. A. FISCHER[3], Alberto GARBUJO[4,*], Pierdomenico BIASI[4], Gunnar JESCHKE[5], Oliver KRÖCHER[1,2] and Davide FERRI[1]

[1]*Paul Scherrer Institut (PSI), Center for Energy and Environmental Sciences, 5232 Villigen, Switzerland.*

[2]*École Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland.*

[3]*ETH Zurich, Laboratory of Physical Chemistry, 8093 Zurich, Switzerland.*

[4]*Casale SA, Basic Research Department, 6900 Lugano, Switzerland.*

*a.garbujo@casale.ch**

Significance and Relevance

Our work demonstrates i) that the simultaneous Selective Catalytic Reduction of N_2O and NO (N_2O-NO-SCR) is a feasible and promising strategy for concomitant conversion of these pollutants, ii) that dynamic *operando* spectroscopic experiments are essential to extract valuable molecular insights and draw reliable mechanistic considerations and iii) that the reactivity of Fe centers in Fe-exchanged zeolites can be disentangled.

Preferred and 2nd choice for the topic: Automotive and stationary emission control / Fundamental advances in understanding catalysis
Preferred presentation: Oral preferred

Introduction and Motivations

The individual abatement of nitrous oxide (N_2O) and nitric oxide (NO) has received tremendous scientific attention owing to their effects on human health and the environment. Differently, their concomitant conversion under selective catalytic reduction (SCR) conditions was far less investigated despite being crucial to control emissions from NH_3 internal combustion engines and from industrial plants devoted to the production of caprolactam as well as nitric and adipic acids.[1] In order to explore the feasibility of the combined SCR of N_2O and NO by NH_3 (N_2O-NO-SCR), to rationalize its reaction mechanism and to isolate the reactivity of active Fe centers in a commercial Fe-exchanged zeolite catalyst (Fe-FER), we monitored the red-ox processes and the dynamics of adsorbed species combining catalytic and transient spectroscopic experiments employing the modulated excitation (ME) approach.[2]

Materials and Methods

The Fe-FER catalyst was provided by CASALE SA.[3] Activity tests were conducted between 200 and 500 °C in a feed of 500 ppm NO, 500 ppm NH_3, 3 vol% O_2 and 0.3 vol% H_2O/N_2 with no N_2O (NO-SCR) or 300 ppm N_2O (N_2O-NO-SCR). N_2O conversion was also monitored under reference conditions of 300 ppm N_2O/N_2 in i) N_2 ii) 500 ppm NO/N_2 and iii) 500 ppm NH_3/N_2. Reactants and products were analyzed using an FTIR spectrometer. Equivalent *operando* X-ray absorption spectroscopy (XAS), electron paramagnetic resonance (EPR) and infrared spectroscopy in diffuse reflectance mode (DRIFTS) experiments were performed by repeatedly adding or cutting-off 1000 ppm N_2O/Ar over Fe-FER equilibrated in i) Ar, ii) 1000 ppm NO/Ar and iii) 1000 ppm NO + 1000 ppm NH_3 + 3 vol% O_2/Ar at 400 °C. An on-line mass spectrometer (MS) monitored the gas concentrations.

Results and Discussion

Catalytic experiments indicated enhanced NO conversion above 300 °C in presence of N_2O. The on-set of this beneficial effect of N_2O coincided with the on-set of N_2O conversion under N_2O-NO-SCR conditions, which also provided highest N_2O conversion compared to reference conditions. Time-resolved XAS spectra (Fe K-edge) showed a shift of the absorption edge towards high energy upon N_2O addition to the NO-SCR feed (Fig. 1a). The spectra obtained by phase sensitive detection,[4] showed an increased contribution of the pre-edge associated with Fe^{3+} species (7115 eV) at the expenses of Fe^{2+}

thus indicating a higher average oxidation state in the presence of N_2O (Fig. 1b). The complementary EPR spectra demonstrated that this phenomenon is related to the Fe^{2+}/Fe^{3+} oxidation of monomeric Fe centers in β- and γ-cationic positions (Fe_β and Fe_γ) possessing a distorted square planar and a tetrahedral coordination, respectively (Fig. 1c),[5] and which are also kept in a reversible red-ox active state during N_2O-NO-SCR (Fig. 1d). Reference experiments showed that this reversible red-ox dynamics occurs because of their involvement in processes of N_2O activation (Fe_β) and NO oxidative transformation (Fe_γ). Equal phase-resolved DRIFTS experiments (Fig. 1f) revealed the formation of Fe_β^{3+}-OH and simultaneous consumption of NO adsorbed on Fe_γ^{2+} during N_2O addition. Enhanced consumption of NH_3 adsorbed on Brønsted sites ($NH_{3,BAS}$) also occurred, but was delayed compared to the kinetics of the Fe_γ^{2+}-NO and Fe_β^{3+}-OH signals.

The combination of these results enables to propose the following rationale: i) N_2O is activated on square planar isolated Fe_β^{2+} sites in form of Fe_β^{3+}-OH, ii) Fe_γ^{2+}-NO species drives utilization of Fe_β^{3+}-OH, promoting iii) the Fe_β^{3+}-OH/ Fe_β^{2+} red-ox transition and the oxidative activation of Fe_γ^{2+}-NO to Fe_γ^{3+}-HONO. Finally, iv) Fe_γ^{3+}-HONO is reduced to Fe_γ^{2+} by reactive $NH_{3,BAS}$ producing N_2 and water through NH_4NO_2 and closing the catalytic cycle.[2]

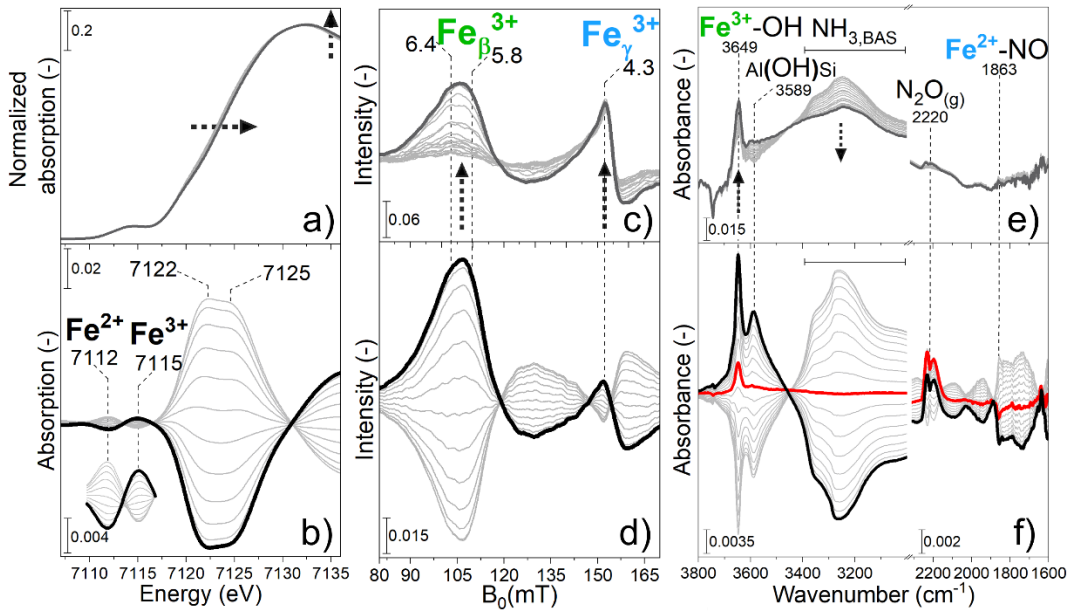


Figure 1. Averaged time-resolved (a, c, e) and phase-resolved (b, d, f) operando XAS (a, b), EPR (c, d) and DRIFT (e, f) spectra of Fe-FER during pulses of 1000 ppm N_2O/Ar in 1000 ppm NO, 1000 ppm NH_3 and 3 vol% O_2/Ar at 400 °C. The coloured spectra in b), d) and f) serve to guide the eye. The red spectrum in f) emphasizes kinetic differences.

References

1. S-J. Lee, R. Soo, K. Byung-Moon, M. Seung-Hyun, *Int. J. Greenh. Gas Control.* **2011**, *5*, 167.
2. F. Buttignol, J.W.A. Fischer, A. H. Clark, , et al., M. Elsener, A. Garbujo, P. Biasi, I. Czekaj, M. Nachtegaal, G. Jeschke, O. Kröcher and D. Ferri, *Nat. Catal.* **2024**
3. F. Buttignol, D. Rentsch, I. Alxneit, A. Garbujo, P. Biasi, O. Kröcher, D. Ferri, *Catal. Sci. Technol.* **2022**, *12*, 7308.
4. A. Urakawa, T. Burgi, A. Baiker, *Chem. Eng. Sci.* **2008**, *63*, 4902.
5. E. Berrier, O. Ovsitser, E. Kondratenko, M. Scwidder, W. Grüner, A. Brückner *J. Catal.* **2007**, *249*, 67.

Acknowledgements

We thank the Paul Scherrer Institut and Casale SA for funding and the Paul Scherrer Institut for beamtime allocation at the SuperXAS beamline (Swiss Light Source). We are grateful to Poland's high-performance Infrastructure PLGrid ACK Cyfronet AGH for providing computer facilities and support within computational grant plgzeodesign24.

Upcycling degraded Li(Ni-Co-Mn)O_2 cathodes to highly active thermal catalyst via lithium pre-extraction method for air pollutant abatement

Sang Woo Byun[1], Hyeonwoo Shin[1], Wonseok Choi[1], Jinju Song[2], Dokyeong Han[2], Jiyoung Ma[2], Jayoung Kim[2], Seok Hyun Song[2], Jung-Je Woo[2] and Sung Bong Kang[*, 1]

[1] *Gwangju Institute of Science and Technology, 123 Cheomdan-Gwagiro, Gwangju 61005, South Korea*

[2] *Gwangju Clean Energy Research Center, Korea Institute of Energy Research (KIER), Gwangju 61003, South Korea*

** e-mail: sbkang@gist.ac.kr*

Significance and Relevance

This study presents a novel upcycling strategy of NCM622 ($Ni_{0.6}Co_{0.2}Mn_{0.2}O_2$) layered transition metal oxide (LTMO) into highly active thermal catalyst for numerous pollutant abatement. Unlike conventional recycling methods mainly focused on metal recovery, our approach provides an upcycling pathway of direct transformation of NCM to thermal catalyst via simple selective Li pre-extraction followed by heat-treatment. This process significantly enhances catalytic performance by increasing surface area and generating new active sites, well-suited for environmental catalysis. This innovative strategy significantly reduces the need for chemical processing while enabling complete recycling of valuable metals, offering dual benefits of environmental protection and resource sustainability.

Preferred and 2nd choice for the topic: 1st Automotive and stationary emission control, 2nd Air cleaning and combustion
Preferred presentation: Oral only

Introduction and Motivations

Given the rapid growth of the broader electrical industries, recycling massive volume of LTMO cathode material in spent lithium-ion batteries presents a significant challenge for both environmental protection and resource sustainability[1]. To date, numerous researchers have proposed solutions for closed-loop and sustainability to address these demands. Mature strategies in industrial scale including pyrometallurgy and hydrometallurgy would somewhat meet this requirement through high-temperature combustion or chemical leaching[2]. As known, however, these are severely limited by low metal recovery rates, toxic by-products, and most critically, extremely low energy efficiency. Under these constraints, research on the recycling of spent cathode materials has expanded beyond closed-loop recycling to explore the potential of the upcycling.

The spent NCM can be upcycled into various high-value products including catalyst; Indeed, NCM holds significant potential as it is composed of transition metals widely used as active metal in thermal catalyst. However, considering the environmental catalysts under actual operating conditions, the low surface area (~4 m^2/g) and the non-reducible, super-stable structure of NCM shows significant limitations to the catalysis. Herein, our study demonstrates a direct upcycling pathway of spent NCM cathodes into superior environmental catalyst through simple Li pre-extraction and oxidative heat-treatment. Through comprehensive catalytic characterization, we identified that delithiated NCM622 undergoes aggregation via oxidative heat treatment, leading to the formation of novel pore structures and active sites derived from thermal stabilization. The upcycled NCM catalyst demonstrated outstanding performance in diverse reactions including CH_4/NH_3/CO oxidation and CO_2 utilization etc., highlighting the potential as versatile environmental catalyst. This work highlights a sustainable and efficient pathway for resource recovery and air pollutant abatement, addressing key challenges in conventional recycling.

Materials and Methods

The NCM622 used in this study was purchased from commercial LIBs cathode. The delithiation process was conducted in two steps: first, NCM622 was stirred in a solution of ACN and NO_2BF_4. Then, the sample was carefully recovered through vacuum filtration followed by repeated washing. All catalytic reaction and heat-treatment were performed in a packed-bed reactor equipped with in-situ FT-IR. Prior to each reaction, catalyst was pretreated at 500 °C for 1 hour under a gas flow consisting of 5% O_2, 5% H_2O with balance N_2.

Results and Discussion

The pristine NCM622 sample (namely, LNCM622) was converted into delithiated NCM622 through the above-mentioned process. The Li removal efficiency was confirmed via ICP analysis, >98% of Li was removed in all NCM622 samples (from 1.01 to 0.02 wt.%). Figure 1 (a) shows the difference of CH_4 oxidation performance between LNCM622 and NCM622 catalyst. Clearly shown, LNCM622 exhibited no CH_4 oxidation activity at all, whereas delithiated NCM622 demonstrated a dramatic improvement in catalytic oxidation performance. As known, CH_4 oxidation is typically challenging on non-PGM based catalyst, especially in the presence of H_2O. However, the delithiated NCM622 showed complete CH_4 oxidation at 600 °C and T_{50}=480 °C, outperforming most of the previously reported non-PGM based catalyst. Beyond CH_4 oxidation, we also applied NCM622 catalyst to various reactions, including CO and NH_3 oxidation, CO_2 hydrogenation, and NH_3 decomposition. The reaction results demonstrated that NCM622 achieved superior catalytic performance for all these reactions.

To investigate the origins of this enhanced catalytic performance, comprehensive characterizations including BET, TEM, EXAFS and series of temperature programmed experiments were conducted. Two key insights emerged from these characterizations: 1) the pre-extraction of lithium contributes to the thermal destabilization of the LTMO structure in NCM622. 2) the defects induced by Li pre-extraction act as vacancies over the LTMO framework, inducing enhanced surface area and redox properties during thermal stabilization. The most pronounced result of the NCM622 during the delithiation and heat-treatment is shown in Figure 1(b); the BET isotherm data. Both LNCM622 and NCM622 exhibit the typical N_2 adsorption-desorption trends of mixed metal oxide, with extremely low specific surface areas. However, the 500 °C heat-treated NCM622 sample show significant changes, including nearly tenfold increase in S_{BET} (3.9 to 41.2 m^2/g) and the formation of mesopore structure, indicating notable morphological transformation. These porous structure via top-down approach is regarded as an essential characteristic for environmental catalysts, which must handle large-scale continuous pollutant streams. Moreover, characterizations including H_2-TPR, XRD, and EXAFS, revealed that during the heat-treatment of NCM622, nickel undergoes controlled aggregation into well-dispersed NiO. These NiO species serve as newly formed active sites, substantially contributing to enhanced redox property. These findings not only establish a framework for the sustainable upcycling of NCM but also guide a pathway for the development of cost-effective, high-performance environmental catalyst.

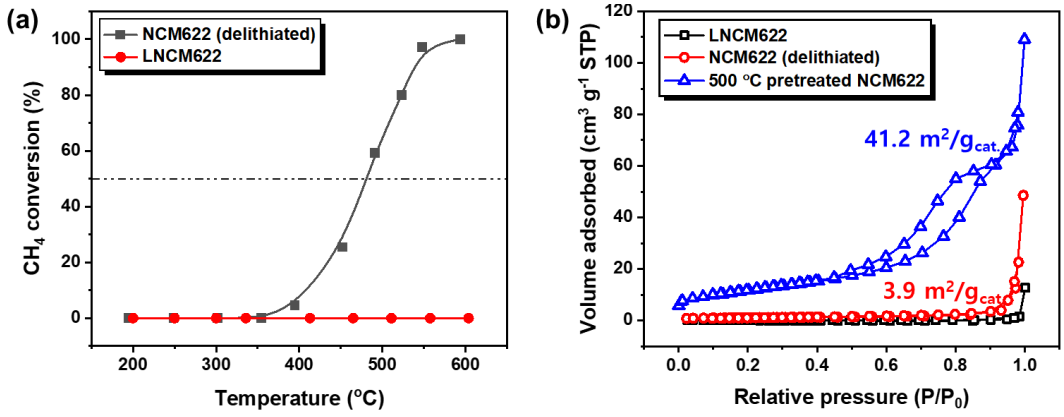


Figure 1. (a) catalytic CH_4 oxidation activity of LNCM622 and NCM622. Reaction conditions: 2000 ppm CH_4, 5% O_2, 5% H_2O in balance N_2, S.V.: 100,000 hr^{-1}. (b) BET analysis of N_2 adsorption-desorption isotherm of LNCM622, NCM622 and 500 °C pretreated NCM622

References

1. C. Xing, M. Yao, L. Fei, *Energy Storage Materials* **2024**, 103636.
2. B. Makuza, Q. Tian, X. Guo, K. Chattopadhyay, D. Yu, *Journal of Power Sources* **2021**, 491, 229622.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. RS-2023-00282392, 2021R1C1C1005404 and 2021R1A5A1028138).

H_2-SCR over 0.3%Pt/5%SiO_2-Al_2O_3 catalyst: investigations in the reaction pathways.

Amira BEN ATTIA[1], Fabien CAN[1], Xavier COURTOIS[1*]
[1] *IC2MP, Université de Poitiers-CNRS, 4 rue Michel Brunet TSA 51106 86073 Poitiers Cedex 9, France.*
** xavier.courtois@univ-poitiers.fr*

Significance and Relevance

The pathways and mechanistic aspects of the H_2-SCR on platinum-based catalysts remain a topic of debate. In this study, we investigated the reaction pathways over a low-loaded supported platinum catalyst depending on the temperature. Our results indicate that NO decomposition occurs mainly below 100 °C, predominantly yielding N_2O. The formation of NH_3 is observed from 70 °C and the NH_3-SCR reaction can occur, but only in the 70-120 °C temperature range, leading mainly to N_2O. Importantly, at temperatures exceeding 120 °C, catalytic activity is mainly driven by the NH_3 oxidation by O_2. To our knowledge ammonia oxidation has not previously been recognized as the main reaction in H_2-SCR reaction pathways.

Preferred topic: **Automotive and stationary emission control**.
2nd choice for the topic: Air cleaning and combustion.
Preferred presentation: **Oral preferred** or Short Oral.

Introduction and Motivations

H_2 internal combustion engine (H_2-ICE) could serves as a viable clean solution for heavy vehicles and could significantly contribute to decarbonizing the transport sector. However, a deNO_x treatment may be necessary. One attractive approach is to implement a H_2-SCR after-treatment system. According to the literature, the H_2-SCR mechanism can be divided into two distinct routes, namely (i) the NO adsorption/dissociation based on a Langmuir-Hinshelwood mechanism and (ii) the oxidation–reduction pathways.[1] Regardless of the mechanism considered, a typical volcano shaped curve in NO_X conversion is obtained. This phenomenon occurs because the competitive H_2 combustion reaction is intensifies as the temperature rises, particularly above 150 °C on precious metals.
The oxidation–reduction mechanism the NO reduction process involves complex reactions between gaseous NO or weakly adsorbed oxidized species (NO^-, NO_2^-, NO_3^-) and adsorbed reduced N-compounds (NH_X).[2] In this study, we investigate the reaction pathways of the H_2-SCR over a low-loaded platinum-based catalyst, with a special focus on (i) the role of NH_3 as possible intermediate species and (ii) the origin of undesired N_2O emission.

Materials and Methods

The 0.3%Pt/5%SiO_2-Al_2O_3 catalyst was prepared using a silica-alumina support provided by Sasol and previously hydrotreated under synthetic air with 10 % H_2O at 700 °C, 4 h (296 $m^2\ g^{-1}$). Platinum was introduced *via* wet impregnation using $Pt(NH_3)_2(NO_2)_2$ salt. After drying, the resulting powder was treated under N_2 at 700 °C, 4 h and finally hydrotreated at 600 °C, 4 h (Pt dispersion: 35 %).

The catalytic behaviour of the sample (30 mg) was investigated using various reaction mixtures, as depicted in Table 1. The feed gas and effluent compositions were monitored using online MKS 2030 Multigas infrared analyser for NO, NO_2, N_2O and NH_3. Additionally, a Pfeiffer Vacuum mass spectrometer was used to record the H_2 signal. The N_2 formation was calculated based on the assumption that only NO, NO_2, N_2O and NH_3 were formed as N-compounds.

Table 1. Reactional mixtures depending on the type of catalytic test (total flow: 150 mL min^{-1}).

Catalytic test	NO (ppm)	NH_3 (ppm)	H_2 (%)	O_2 (%)	N_2
H_2-SCR	400	-	1	2	balance
NO+H_2 reaction	400	-	1	-	balance
NH_3-SCR	400	400	-	2	balance
NH_3 oxidation	-	400	-	2	balance

Results and Discussion

As expected, the NO_X conversion in H_2-SCR conditions (Fig. 1A) showed a volcano-shaped curve. The conversion started below 50 °C, with N_2O as main product. Interestingly, despite a high WHSV of 300 L h^{-1}/g_{cata} (30 mg catalyst, total flow rate of 150 mL min^{-1}), some ammonia was detected from 70 °C, with a maximum yield recorded near 100 °C. At this temperature complete NO_X conversion was achieved, with N_2 emerging as the main reduction product. At higher temperatures, a secondary N_2O emission was observed. To explain these complex profiles, especially the role of NH_3 as possible intermediate and the origin(s) of the undesired N_2O emission, various reaction mixtures were used to study the NH_3 formation and its reactivity.

Removing oxygen ($NO+H_2$ reaction, Fig. 1B) had no influence in the 50-100 °C temperature range, indicating that the actives sites were mainly covered by NO_X species, with N_2O as the main reaction product (accordingly, H_2 conversion was shifted to lower temperature when NO was removed from the reaction mixture, results not shown). The NH_3 emission started near 70 °C, consistent with the H_2-SCR conditions (Fig. 1A). Considering the ammonia reactivity, the NH_3-SCR (Fig. 1C) can occur from 70 °C, exhibiting significant activity from 100 °C. However, this reaction within the H_2-SCR process can only proceed when both NH_3 and NO_x are available simultaneously, which is possible only in a very narrow range (Fig 1A, also confirmed varying the involved catalytic mass from 5 to 200 mg). Moreover, the distribution of N_2 and N_2O in the 100-350 °C temperature range in NH_3-SCR did not match with the results observed in H_2-SCR (Fig. 1A). On the contrary, the second N_2O emission wave observed in H_2-SCR (Fig 1A) correlated very well with the NH_3 oxidation by O_2, which led mainly to N_2 (Fig. 1D). An overview of the H_2-SCR reaction pathways depending on the temperature is proposed in Fig. 1E, highlighting the NH_3 reaction routes.

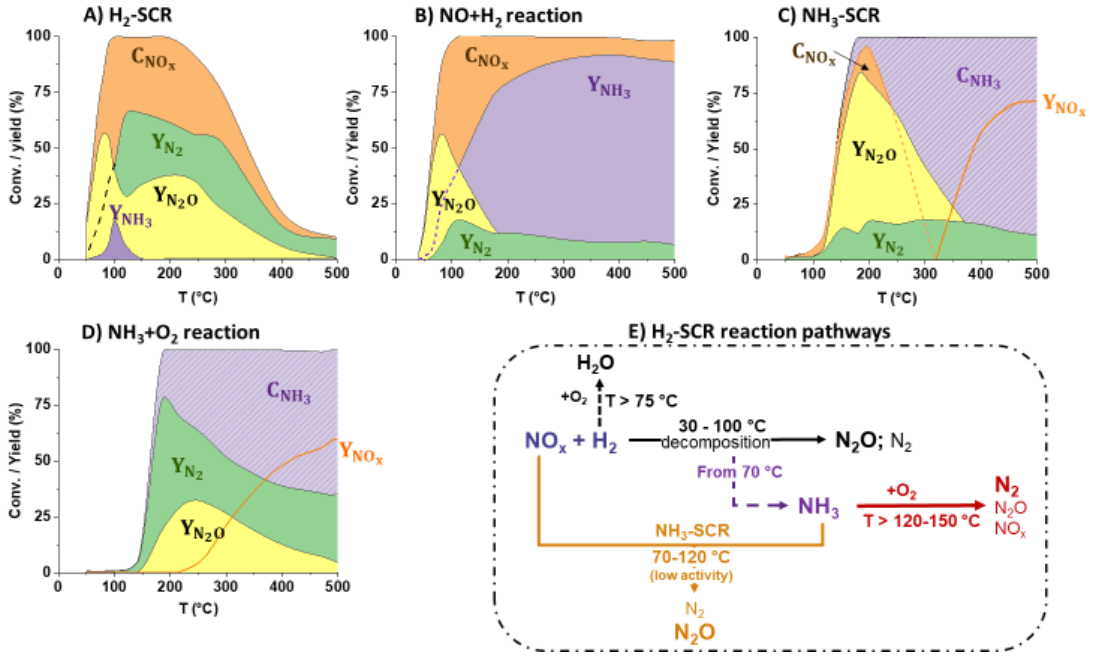


Figure 1: 0.3%Pt/5%SiO_2-Al_2O_3 catalytic behavior (C: conversion; Y: yield) depending on the reaction mixture reported in Table 1 and proposed H_2-SCR reaction scheme depending on the temperature.

References

1. Z. Liu, J. Li, S. Ihl Wooc, *Energy Environ. Sci.* **2012,** *5,* 8799-8814.
2. R. Burch, M. D. Coleman., *J. Catal.* **1999**, 188, 69-82.

Acknowledgements

The authors gratefully acknowledge the French National Agency for Research (ANR, H to Clean Project, ref. ANR-21-CE05-0012-01), the Regional Council of Nouvelle Aquitaine (DeNOx-DeCarb project, AAPR2022-2021-17214210), the French Ministry of Research and the European Regional Development Fund (ERDF) for financial supports.

Site-specific monomeric Fe sites catalyze the N_2O decomposition reaction

Daniel C. Cano-Blanco[1], Jörg W. A. Fischer[3], Filippo Buttignol[1], Gunnar Jeschke[3], Oliver Kröcher[1,2], Davide Ferri[1]
1 Paul Scherrer Institute, 5232 Villigen, Switzerland; 2 Institute for Chemical Science and Chemical Engineering, École polytechnique fédérale de Lausanne (EPFL), Lausanne, Switzerland; 3 Department of Chemistry and Applied Biosciences, ETH Zurich, 8093 Zurich, Switzerland
**daniel.cano-blanco@psi.ch*

Significance and Relevance

Determining the nature of active sites in complex catalysts such as Fe-exchanged zeolites is challenging due to the variety of coordination environments Fe ions can adopt. In this work, we present an *operando* multi-spectroscopy investigation, complemented by spectroscopic-based kinetic analyses, to elucidate the mechanistic details of N_2O decomposition over Fe-SSZ-13. We demonstrate the site selectivity of the process, involving the redox of specific Fe ions, where the reduction half cycle is the rate-determining step. We highlight the value of *operando* spectroscopy to draw structure-activity relations and elucidate kinetic details, offering insights to guide efforts in the development of Fe-zeolites for use in advanced after-treatment processes, such as N_2O abatement in NH_3 engines.

Preferred and 2nd choice for the topic: Fundamental advances in understanding catalysis, Automotive and stationary emission control.
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

In the context of energy transition and new frontiers in environmental catalysis, N_2O has emerged as a significant challenge for next-generation emission control technologies. Fe-containing zeolite catalysts exhibit remarkable activity for the decomposition of N_2O and the selective catalytic reduction of nitrogen oxides by NH_3.[1] Extensive research has been dedicated to these materials,[2] yet most characterizations, assignment of active sites, and structure-activity relationships relied predominantly on ex situ experiments. This often led to conflicting interpretations and assignments, due to the presence of numerous spectator species and the dynamic nature of the active centers under operando conditions. To address these challenges, we have dedicated efforts to the investigation of Fe-exchanged zeolites using a comprehensive set of bulk, site-selective, and vibrational spectroscopies, combined with modulated excitation (ME) and phase-sensitive detection (PSD). This approach allowed us to precisely track Fe species, identify intermediate species, and unambiguously assign the active sites.

Materials and Methods

Fe-SSZ-13 was synthesized via a one-pot hydrothermal method and thoroughly characterized.[3] Catalyst performance was evaluated in a plug-flow reactor. The dynamics, speciation, and nature of Fe under conditions representative of N_2O decomposition were elucidated using *operando* resonance inelastic X-ray scattering (RIXS), high-energy resolution fluorescence-detected X-ray absorption spectroscopy (HERFD-XAS), X-ray emission spectroscopy (XES), electron paramagnetic resonance (EPR), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and diffuse reflectance UV-Vis spectroscopy (DRUV). ME experiments consisted in the periodic variation of the concentration of N_2O while recording spectra simultaneously.

Results and Discussion

Ex situ EPR and DRUV revealed the coexistence of distinct Fe species within the zeolite. Despite this complex speciation, *operando* DRUV experiments enabled tracking of the redox dynamics ($Fe^{2+} \leftrightarrow Fe^{3+}$) and further indicating that only a fraction of the species participates actively in the full catalytic cycle (**Fig 1a**). Kinetic analyses of *operando* DRUV and EPR data showed that both oxidation half-cycle (OHC) and reduction half-cycle (RHC) proceed via 1st order reactions, with the kinetic constant of oxidation (k_{ox}= 0.034 s^{-1}) exceeding the reduction rate constant (k_{red}= 0.013 s^{-1}), thus confirming the

rate-determining nature of the RHC. Quantitative pre-edge analysis of the HERFD-XAS data suggests that Fe may adopt an octahedral coordination, which appeared to be distorted in the presence of N_2O, as evidenced by the feature at 7.12 keV in the PSD data (**Fig. 1b**). *Operando* EPR further demonstrated that the N_2O decomposition reaction is site-selective, involving only the isolated Fe species located in the 6-membered rings of the β cationic exchange sites of the zeolite ($Fe_\beta^{2+} \leftrightarrow Fe_\beta^{3+}$; **Fig. 1b**). DRIFTS identified Fe_β^{3+}-OH (**Fig. 1b**), likely as manifestation of the $[FeO]^{2+}$ moiety, previously reported as intermediate species.[4] Additionally, spin-selective HERFD-XAS ruled out the presence of Fe^{4+}=O, suggesting a radical intermediate of oxidation state 3+ ($Fe_\beta^{2+} \leftrightarrow Fe_\beta^{3+}$-O$^{\cdot} \leftrightarrow Fe_\beta^{3+}$-OH). The evolution of isolated high-spin Fe_β^{3+} sites in the OHC and the RHC was further probed using high-time resolution *operando* EPR (**Fig. 1c**), which gave access to the apparent activation energies (Ea_{app}) of the RHC (ca. 138 kJ·mol^{-1}) and the OHC (ca. 34 kJ·mol^{-1}).

Our results reveal a strong correlation between the kinetics of the monomeric Fe centers and the N_2O decomposition kinetics (ca. 138 kJ·mol^{-1}), thus allowing the consistent assignment of the global reactivity of the catalyst to the Fe_β centers.

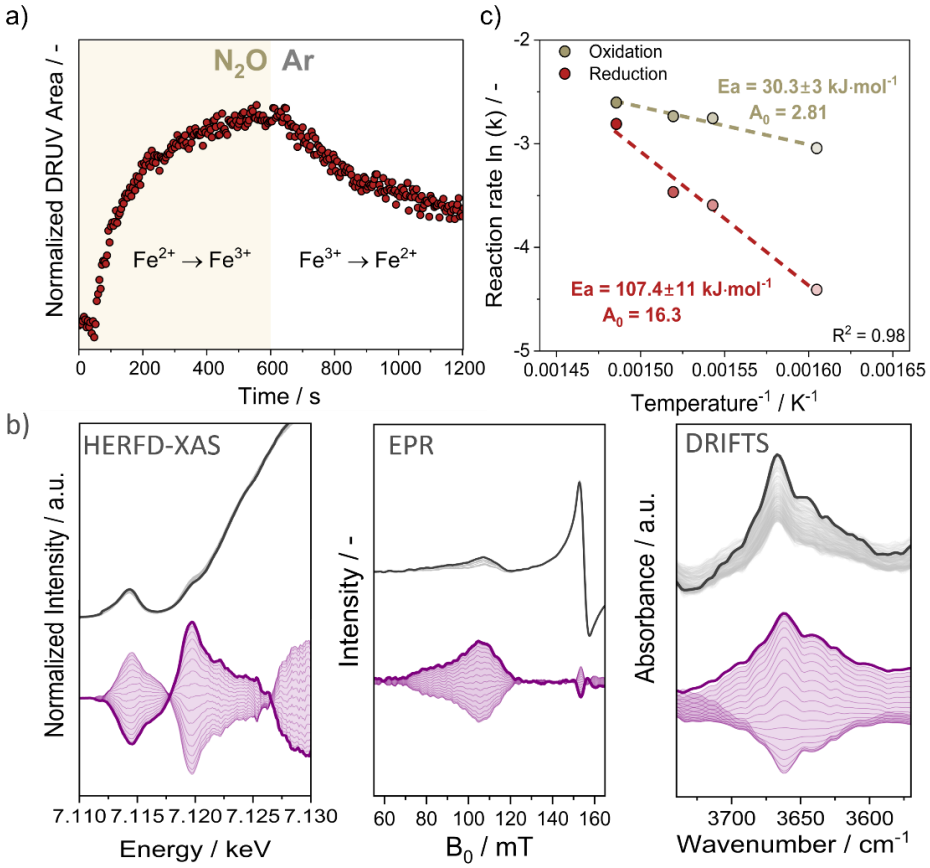


Figure 1. Characterization of catalytic N_2O decomposition. (a) temporal evolution of UV-vis spectra at 400°C; (b) time and phase-resolved HERFD-XAS, EPR, DRIFTS spectra obtained during the ME experiment at 400°C; (c) Arrhenius plots obtained from selectively monitoring Fe_β by EPR.

References

1. K.A. Dubkov et al., J. Catal. **2002**, 207, 341.
2. J. Perez-Ramírez et al., J. Catal. **2004**, 223,13.
3. M.L. Bols et al., J. Am. Chem. Soc. **2021**, 16243, 143.
4. E. Berrier et al., J. Catal. **2007**, 249, 67.

Acknowledgements

We thank the FVV and Swiss Federal Office of Energy (SFOE) for funding the project and the European Synchrotron Radiation Facility (ESRF) for provision of synchrotron radiation facilities.

Structural parameters for high activity and stability of Pd/CeO_2 CH_4 oxidation catalysts

D. Zengel[1], V. Marchuk[1], M. Kurt[1], F. Maurer[1], A. Salcedo[2], C. Michel[2], D. Loffreda[2], M. Aouine[3], T. Epicier[3], S. Loridant[3], P. Vernoux[3], M. Casapu[1]*, J.-D. Grunwaldt[1]

[1]*Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany*

[2]*ENS de Lyon, CNRS UMR 5182, Laboratoire de Chimie, Lyon, France*

[3]*Institut de Recherches sur la Catalyse et l'Environnement de Lyon, CNRS UMR5256, Université de Lyon, Lyon, France*

**maria.casapu@kit.edu*

Significance and Relevance

Due their high costs, increasing the efficiency of the noble metal based catalysts is highly important for numerous applications including emission control. A systematic study on the influence of noble metal loading relative to the specific surface area of ceria supports on the activity and stability of Pd-based methane oxidation catalysts is reported. The results show a clear correlation between the noble metal coverage as single site layer and the evolution of the catalyst under reaction conditions. The highest noble metal efficiency and catalyst stability was identified for loadings close to the monolayer coverage [1].

Preferred and 2nd choice for the topic: Automotive and stationary emission control; Air cleaning and combustion

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

In combination with noble metal (NM) as active species, ceria is one of the most applied supports in heterogeneous catalysis. As strongly interacting and functional materials, CeO_2 and CeO_2-ZrO_2 are mostly used to prevent the noble metal sintering and buffer the oxygen concentration in emission control. Additionally, the perimeter sites at the interface with the noble metal particles were found to directly contribute to oxidation reactions[2]. However, the strong NM-CeO_2 interaction leads also to the formation of single sites or highly dispersed NM species, which have been shown to be less active[3-4]. Particularly for reactions involving the exposure to high temperatures such a deactivation mechanism needs to be considered. Although the re-formation of noble metal particles can be induced by reductive treatments, this approach is not favoured during real applications. With our study we propose an alternative path for controlling the formation of Pd particles in CeO_2-based methane oxidation catalysts by adjusting the noble metal loading and the support specific surface area to slightly exceed the single site monolayer coverage concentration.

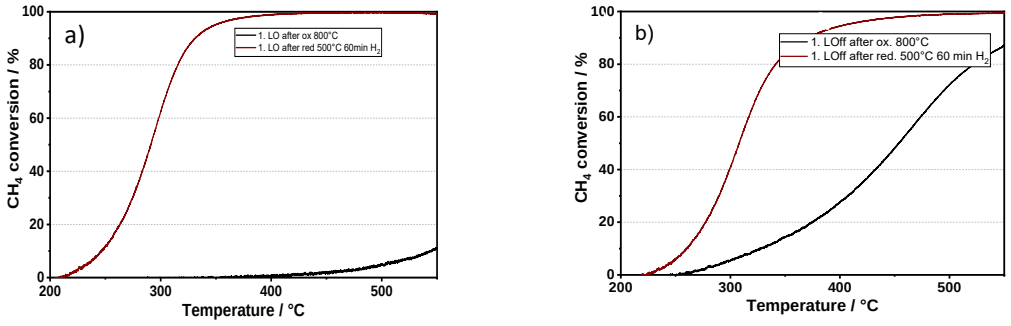


Figure 1. CH_4 oxidation activity of Pd/CeO_2 catalysts with 20% (a) and 120% (b) noble metal coverage pre-treated at 800°C in oxidizing conditions (black line) and H_2 pre-reduced at 500°C (red line). Gas mixture: 3200 ppm CH_4, 0-5%H_2O, 10% O_2 in N_2; WHSV 20000 L/$g_{NM}^{-1}h^{-1}$ (high WHSV). [1]

Materials and Methods

A series of Pd catalysts with noble metal loadings of 1-3 wt.% were supported on CeO_2-based materials with different specific surface areas (30-120 m^2/g) by incipient wetness impregnation. To disperse Pd homogenously over the CeO_2 surface, the obtained samples were calcined for 10 h at 800 °C in static air. The resulting catalysts were characterized by complementary *ex situ* and *in situ/operando* characterization methods including XRD, ETEM/EDXS, DRIFTS, XAS and XPS. The variations in the sample characteristics depending on the catalyst pre-treatment are supported by DFT calculations. Catalytic tests were conducted for the granulated samples (125 – 250 µm) in a plug-flow reactor while measuring the reaction products with an FTIR Gas Analyzer (MKS).

Results and Discussion

The results obtained indicate a pronounced increase in the CH_4 oxidation activity by applying a reductive treatment to Pd/CeO_2 samples containing single noble metal sites and small clusters. Larger particles and a higher catalyst stability were obtained by using CO for the reductive treatment instead of H_2. Moreover, by adjusting the noble metal loading per surface area unit of CeO_2-based supports, the spreading of the entire noble metal amount as inactive single sites was prevented. For Pd concentrations slightly exceeding the theoretical single site monolayer coverage an improved activity was measured already in the as prepared catalyst state (Fig. 1b, after oxidation at 800°C for 10h), which was combined with a higher stability during the following activity cycles. In contrast, for lower noble metal loadings, the activity gained after the pre-reduction treatment shows a rapid decay due to the noble metal redispersion. The formation or redispersion of Pd nanoparticles depending on the gas atmosphere and temperature was monitored during ETEM measurements. Further differences in the noble metal structure leading to a higher or lower catalyst activity and durability were uncovered by *in situ* DRIFTS and *operando* XAS characterization, and were additionally supported by DFT calculations[5]. Summarizing, a threshold for Pd concentration on CeO_2-based supports was identified around the monolayer coverage, which ensures an optimal usage of the noble metal and a high stability of the catalyst by preventing excessive sintering or redispersion.

References

1. D. Zengel, V. Marchuk, M. Kurt, F. Maurer, A. Salcedo, C. Michel, D. Loffreda, P. Vernoux, M. Casapu, J.-D. Grunwaldt, *Appl. Catal. B* **2024**, 358, 124363.
2. M. Cargnello, V.V.T. Doan-Nguyen, T. R. Gordon, R. E. Diaz, E.A. Stach, R. J. Gorte, P. Fornasiero, C. B. Murray, *Science* **2013**, 341, 771
3. A. M. Gänzler, B. Betz, S. Baier-Stegmaier, S. Belin, V. Briois, M. Votsmeier, M. Casapu, *J. Phys. Chem*. C **2020**, 124, 20090−20100
4. F. Maurer, J. Jelic, J. Wang, A. Gänzler, P. Dolcet, C. Wöll, Y. Wang, F. Studt, M. Casapu, J. -D. Grunwaldt, *Nat. Catal.* **2020**, 3 (10), 824−833.
5. A. Salcedo, D. Zengel, F. Maurer, M. Casapu, J.-D. Grunwaldt, C. Michel, D. Loffreda, *Small* **2023**, 2300945.

Acknowledgements

The authors acknowledge the financial support from the Agence Nationale de la Recherche (grant No. ANR-19-CE05-0038, PRCI DYCAT project), the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation; grant No. 431423888 DYCAT project and grant NO. 3987/18-1) and KIT for financial support.

Lithium-mediated pathways towards ammonia electroproduction

Anna MANGINI[1], Sara GARCIA-BALLESTEROS[1], Federico BELLA[*,1]
[1]*Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 – Torino, Italy.*
** federico.bella@polito.it*

Significance and Relevance

The proposed work focuses on the electrochemical synthesis of ammonia through lithium-mediated processes inspired by battery technologies. This approach addresses the pressing need for sustainable ammonia production, reducing reliance on energy-intensive Haber-Bosch processes. By integrating advancements in battery science, the study aims to enhance efficiency and scalability, contributing to global efforts in green chemistry and energy transition. The relevance lies in its potential to revolutionize industrial ammonia synthesis, making it more environmentally and economically viable.

Preferred and 2nd choice for the topic: H_2 storage and transportation, green H_2 production, hydrogen vectors / Sustainable and clean energy production and transport

Preferred presentation: Oral only

Introduction and Motivations

Ammonia, produced *via* the Haber-Bosch process for more than 150 10^6 t per year, is responsible of around 1.5% of the global greenhouse gas emissions [1]. It is a fundamental building-block for fertilizers and could represent a future H_2 carrier, but it is still dependent from fossil fuels. To find a delocalized electrochemical process complementary to Haber-Bosch could be a key solution to move towards a renewable-driven NH_3 production.

Nowadays, the lithium-mediated pathway represents the most promising solution in the N_2 reduction reaction challenging field, achieving the highest Faradaic efficiency and NH_3 production rate [2,3]. Different strategies are under evaluation in literature, all exploiting the ability of this metal to bind N_2 even in standard conditions. They could be divided into continuous or step-by-step strategies. In the first, Li^+ ions from the aprotic electrolyte are electrodeposited on the cathode, where N_2 is reduced and protonated into NH_3, directly and in the same environment [4]. In the second case, the electroreduction of N_2 at the cathode has been proposed, and the formation of an intermediate product containing fixated nitrogen is the key step. Only in a second separate step, this intermediate should be protonated into NH_3. To achieve the first step of N_2 activation, the exploitation of a Li-N_2 galvanic cell, inspired by lithium-air batteries, has been proposed in literature to optimize the process efficiency and allow the direct protonation with H_2O [5,6].

Materials and Methods

In both cases, is crucial to study the phenomena at the cathodic electrode-electrolyte interphase, as the aprotic electrolyte inevitably reacts on the active sites, forming a solid electrolyte interphase. This component of the system determines both the selectivity towards NH_3 formation and the stability of the process. Due to the dynamicity of this layer, a critical eye should be adopted for a correct electrochemical characterization and NH_3 quantification of the systems. Our laboratory is currently addressing these challenges within the SuN_2rise project, applying also statistical methods as the design of experiment to optimize the studied factor with a restricted number of experiments.

Results and Discussion

To fasten the comprehension and optimization of the complex lithium-mediated nitrogen reduction system, for the first time a multivariate approach is proposed as a powerful tool to reduce the number of experiments in comparison with the classical one-factor-at-a-time approach. Doehlert design and surface response methodology are employed to optimize the electrolyte composition for a batch

autoclaved cell. The method is validated with the common $LiBF_4$ salt, and the correlations between the FE and the amount of lithium salt and ethanol as proton donor are elucidated, also discussing their impact on the solid electrolyte interphase (SEI) layer. Moreover, a new fluorinated salt is proposed (*i.e.*, lithium difluoro(oxalate) borate (LiFOB)), taking inspiration from lithium batteries. This salt is chosen to tailor the SEI layer, with the aim of obtaining a bifunctional interfacial layer, both stable and permeable to N_2, the latter being an essential characteristic for batch systems. The SEI layer composition is confirmed strategic and its tailoring with LiFOB boosts FE values even at considerably high water content (*i.e.*, 600 ppm).

References

[1] G. Soloveichik, Nat. Catal, **2**, 377–380, 2019.

[2] X. Fu *et al.*, *Science*, **379**, 707–712, 2023.

[3] N. Lazouski *et al*., *ACS Catal.*, **12**, 9, 5197–5208, 2022.

[4] S. Li *et al., Nature*, **629**, 8010, 2024.

[5] A. Mangini *et al., Adv. Energy Mater.,* **14**, 2400076, 2024.

[6] Z. Zhang *et al., Angew. Chem. Int. Ed.*, **58**, 17782–17787, 2019.

Acknowledgements

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No. 948769, project title: SuN$_2$rise).

Innovative CO_2 recycling system with powerful performance for converting GHG: Multi-stage structured catalyst system for methanation, dry reforming and carbon-capture

Choji Fukuhara*, Yuki Yamada, Yu Nakazawa, Hiroshi Akama, Ryo Watanabe
Department of Applied Chemistry and Biochemical Engineering, Graduate School of Engineering, Shizuoka University, 3-5-1 Johoku, Chuo-ku, Hamamatsu, Shizuoka, Japan
** fukuhara.choji@shizuoka.ac.jp*

Significance and Relevance

The multi-stage catalyst reaction system was established for post-treating the greenhouse gas (GHG), which consists of three reaction stages: a CO_2 methanation zone in the first stage, a CH_4 dry reforming (DRM) zone in the second stage, and a solid carbon capture zone in the third stage (a multi-stage system). All stages have a structured reaction system equipped with effective heat and mass transfers abilities (especially, a spiral-type catalyst system), indicating powerful and stable performances even under some mass processing conditions. The constructed system can efficiently convert GHG into some valuable materials such as methane, synthesis gas and solid carbon, contributing to carbon-neutral technology. From a thermodynamic evaluation using exergy, the usefulness of the constructed system was confirmed.

Introduction and Motivations

In order to achieve a carbon-neutral society, there is currently active research focused on developing catalysts and reaction systems that aid in reducing GHG (CO_2, CH_4). This research aims to introduce a novel approach to both reducing and effectively utilizing CO_2. Specifically, the primary goal of this study is to focus on the post-treatment of CO_2 emissions from some industrial processes and establish a comprehensive catalytic system for CO_2 utilization. The established catalytic system consists of three stages: a CO_2 methanation zone in the first stage[1], a CH_4 dry reforming (DRM) zone in the second stage, and a solid carbon capturing zone in the third stage [2,3]. The assessment of the system's characteristics showed that, even at a high flow rate of 2.0 L/min, the system consistently produced synthesis gas (H_2+CO) and efficiently recovered more than 56% of the CO_2 in the form of solid carbon. Furthermore, it was confirmed that the system operates more effectively when the hydrogen content is kept below (H_2/CO_2=2.0-3.0) the stoichiometric ratio of methanation. This modification significantly improves the performance of the DRM and the rate of carbon capturing. Moreover, a thermodynamic assessment of this system suggests that reducing the supplied amount of hydrogen has a beneficial effect on the system's exergy efficiency.

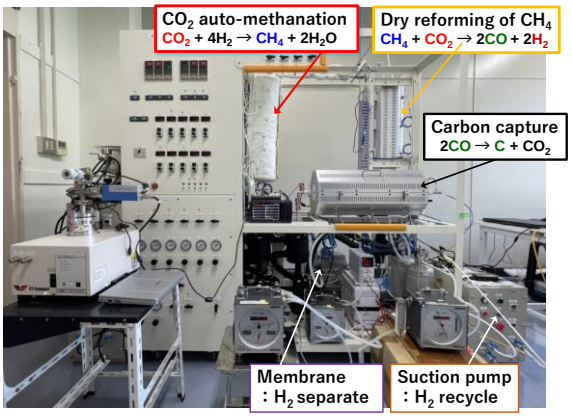


Figure 1 Multi-stage reaction system for converting GHG into useful materials

Reaction system and Structured catalyst

Figure 1 shows the multi-stage reaction system designed to simultaneously reduce CO_2 and produce synthesis gas and solid carbon. The system consists of three reaction parts (first stage: methanation, second stage: DRM, third stage: carbon capture, in series), utilizing various structured catalysts, as depicted in Figure 2. The catalysts were the spiral-type Ni/CeO_2 and/or Ru/CeO_2 for methanation, the spiral-type Ni/CeO_2-Al_2O_3 for DRM and the wall-type Fe-Co-K

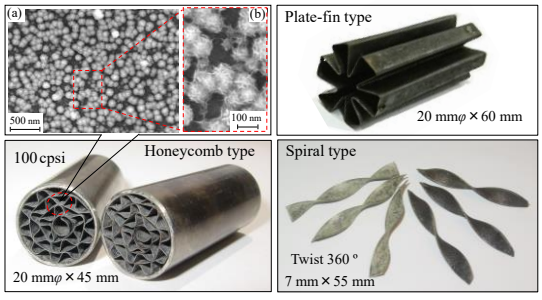


Figure 2 Various structured catalysts used in methanation, DRM and carbon capture

catalyst for carbon capture. All catalysts were prepared on both aluminum substrate and stainless-steel substrate, using the wash-coating and/or the electroless plating. The feeding gas condition was as follows: CO_2 : H_2 : O_2 : N_2 = 20 : 56 : 3 : 21 vol%, with a feeding rate ranging from 1.0 to 10.0 L/min. After reducing each catalyst, reaction was carried out at 25 °C (room temperature) for methanation, 700 °C for DRM, 470 °C for carbon capture.

Results and Discussion

Figure 3 displays typical results from the constructed multi-stage system operating at a feeding gas rate of 2 L/min, highlighting its impressive capability to convert GHG into valuable materials. The CO_2 conversion in methanation zone was approximately 75 % without external heating (at room temp.), and CH_4 was selectively produced with 98% or more. In DRM zone, both CO_2 and CH_4 conversions were 70 % or more, and synthesis gas was produced with H_2/CO= 2.0, which is suitable for the Fischer-Tropsch process. In addition, carbon capture rate was 56 %. From TEM and SEM observations, the captured carbon takes on some fibrous shape with nanotube structures, offering the potential for utilization as functional materials.

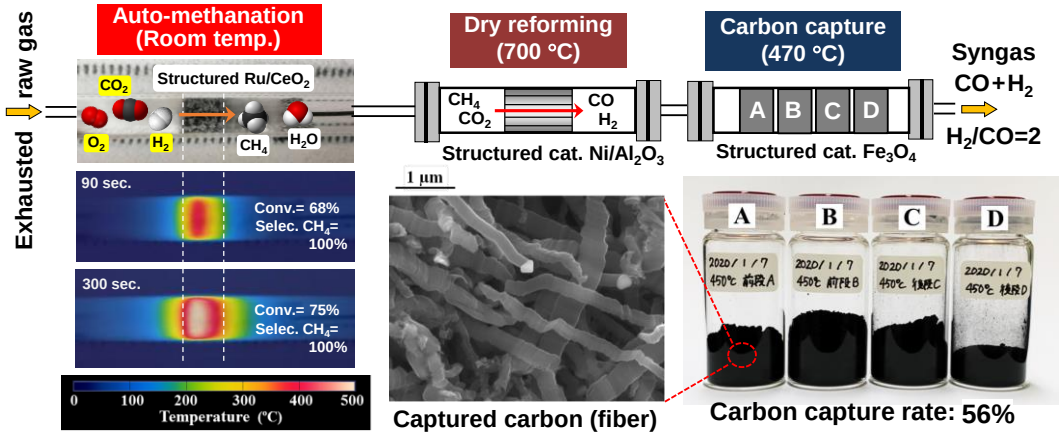


Figure 3 High performance of constructed system for producing syngas and solid carbon from GHG

Figure 4 represents a thermodynamic evaluation of the constructed system using exergy as an index. Methanation process consumes a large amount of hydrogen (H_2/CO_2=2.0-3.0), thereby the system diminished the exergy efficiency. However, by integrating dry reforming and solid carbon capturing processes, such disadvantage of the system was progressively recovered, resulting in the thermodynamic advantage. The system's effectiveness is clearly evident.

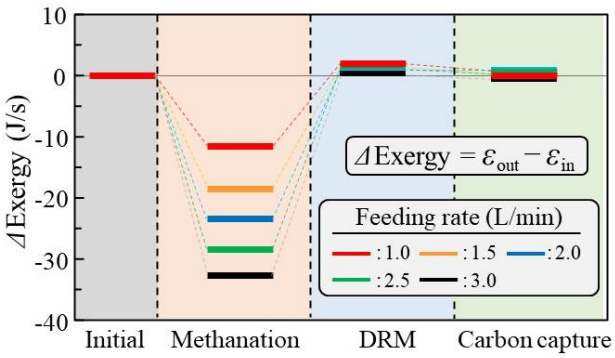


Figure 4 Exergy merit of the multi-stage system

References

1. C. Fukuhara, A. Kamiyama, M. Itoh, N. Hirata, S. Ratchahat, M. Sudoh, R. Watanabe, Chemical Engineering Science, **2020**, *219*, 115589.
2. W. Kawasaki, R. Watanabe, C. Fukuhara, Journal of CO_2 utilization, **2017**, *22*, 91-96.
3. C. Fukuhara, Y. Matsui, M. Tanebayashi, R. Watanabe, Chemical Engineering Journal Advances, **2021**, *5*, 100057.

Acknowledgements

This work was supported by JSPS KAKENHI Grant Numbers 23H00530, 21K18317, 20H00642, Japan.

Mesoporous Ni/La_2O_3 catalyst for highly efficient NH_3 decomposition

Sebastián GAMEZ[1*], Josefine SCHNEE[2] and Eric M. GAIGNEAUX[1]
[1] *Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, Pl. Louis Pasteur 1, 1348 Louvain-la-Neuve, Belgium.*
[2] *Sorbonne Université, Laboratoire de Réactivité de Surface (LRS), CNRS, Campus Pierre et Marie Curie, 4 Place Jussieu, F-75005 Paris Cedex 05, France*
** sebastian.gamez@uclouvain.be*

Significance and Relevance

We report on an advanced synthesis method that combines a complexing agent, a hard template and an exsolution step to produce a high specific surface area catalyst which consists in Ni nanoparticles embedded on La_2O_3. Our catalyst reaches almost complete conversion at 550 °C in NH_3 decomposition with H_2 production rates similar to those reached with expensive doped Ru catalysts. By increasing Ni nanoparticles dispersion on a mesoporous La oxide-based matrix, our catalyst also succeeds keeping high conversions for long periods (i.e. 72 h) demonstrating its unique stability.

Preferred and 2nd choice for the topic: H2 storage and transportation, green H2 production, hydrogen vectors (preferred); Fundamental advances in understanding catalysis (2nd)
Preferred presentation: (Oral only / ***Oral preferred or Short Oral*** / Poster)

Introduction and Motivations

Due to fossil fuels depletion and environmental issues, worldwide societies are looking for new efficient and green energy carriers to replace these carbon-based polluting energy sources.[1] In this regard, hydrogen (H_2) arises as a plausible alternative, but issues related to its handling and storage have blocked its upscaling and application.[1] Hence, current efforts are focused on developing new technologies to efficiently produce H_2 from non-carbon sources with high H_2 content.[2] The most promising candidate is ammonia (NH_3) due to its high H_2 density and easy handling andstorage. Nevertheless, the challenge lies in its decomposition into H_2 since this process is carried out at high temperatures (i.e. > 800 °C).[2] So far, Ru catalysts with basic doping agents can perform this reaction at temperatures below 550 °C.[3] However, since Ru is a scarce and expensive noble metal, we have developed a new synthesis method to produce a high specific surface area Ni catalyst capable of reaching high H_2 production yields at low temperatures without using neither critical element nor doping agent to achieve its high performance.

Materials and Methods

$Ni(NO_3)_2$ and $La(NO_3)_3$ along with citric acid (1:1:2) were dissolved in a ethanol/H_2O (3/1) solution under continuous stirring. The complexing agent (i.e. citric acid) chelates Ni and La cations to facilitate the formation of $LaNiO_3$ perovskite in the following stages. Next, a mesoporous SBA-15 (~900 m^2/g) was added as hard-template to the mixture, which is heated at 60 °C and rotary evaporated to remove the solvents. Thereby, Ni and La cations diffused inside SBA-15 porosity, where during the subsequent calcination at 750 °C they formed a $LaNiO_3$ perovskite. Next the SBA-15 hard-template was removed by washing the solid with a 5 mol/L NaOH solution at 90 °C. The resulting mesoporous high specific surface area perovskite obtained after SBA-15 removal was named $LaNiO_3$-S. The same protocol was used to synthesize a reference bulk perovskite sample without SBA-15 intervention ($LaNiO_3$-B). Samples were all characterized by X-ray diffraction and N_2 physisorption to check the perovskite formation as well as their textural properties. Prior to catalytic tests, samples were exsolved under H_2 atmosphere at 550 °C for 1 h. Ni nanoparticles dispersion was assessed by TEM microscopy along with H_2 chemisorption to correlate the data with the catalytic performances achieved in NH_3 decomposition at a GHSV = 30 000 $mLNH_3/g_{cata}.h$ in a range of 300-650 °C.

Results and Discussion

$LaNiO_3$-B and $LaNiO_3$-S show the same characteristic XRD peaks corresponding to lanthanum nickelate confirming that SBA-15 addition (and its subsequent removal) did not alter the formation of the perovskite structure (and its integrity) (Fig 1a). The main difference is observed in their textural properties since $LaNiO_3$-S displays 50 times the specific surface area reached by $LaNiO_3$-B with a pore size distribution centered on 5 nm (Fig 1c). After exsolution, both samples, now denoted as R-$LaNiO_3$-B and R-$LaNiO_3$-S, present similar textural properties as before, but XRD revealed their structure changed into Ni nanoparticles (NP) on La_2O_3 (Fig 1b-c). TEM analyses confirmed the presence of Ni NP and their embedment on the La oxide, as well as the presence of mesopores in R-$LaNiO_3$-S (as also revealed by N_2 physisorption), while EDS analyses showed a better dispersion of Ni nanoparticles than in the case of R-$LaNiO_3$-B (Fig1 d-e). During catalytic tests R-$LaNiO_3$-S reached almost complete conversion at 550 °C with a H_2 production rate of 29.9 mmol/g_{cat}.min. A gap of 20% in conversion was found amid both catalysts demonstrating that the better Ni dispersion on R-$LaNiO_3$-S greatly improved its catalytic performance (Fig1f). Moreover, this catalyst remained active for 72 h when NH_3 decomposition was carried out at 550 °C, which results from the Ni NP embedment achieved thanks to the exsolution approach. Hence, this novel method builds an efficient and active catalyst without using basic doping agents (e.g. Sr, Mg) or noble metals (e.g. Ru) to produce H_2 in NH_3 thermic decomposition at low temperatures.

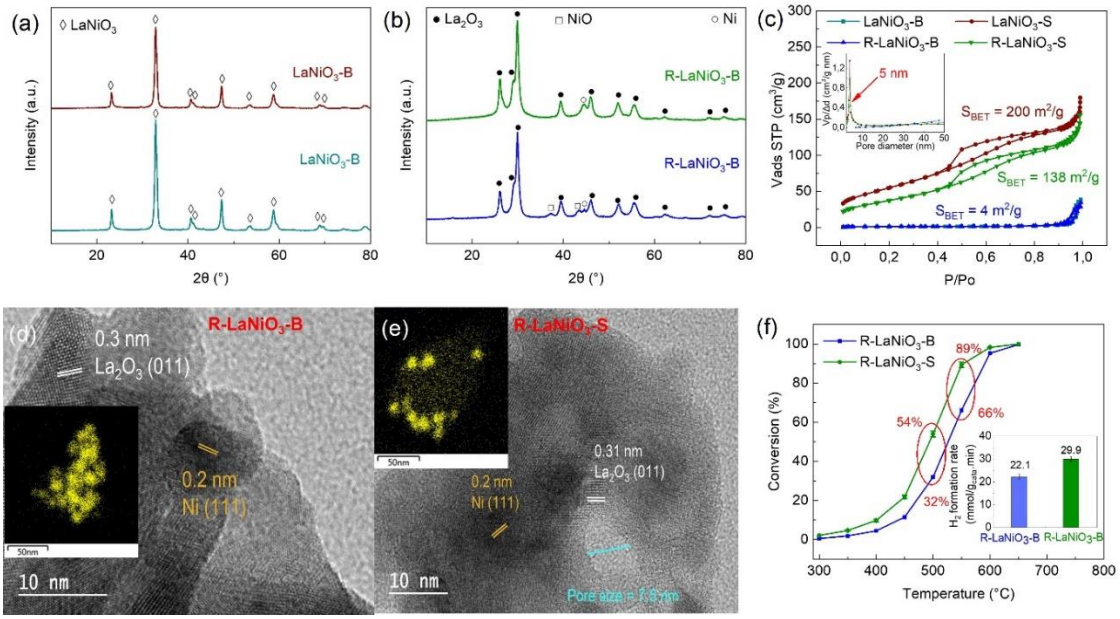


Figure 1. Diffractograms of: a) Perovskites; b) exsolved perovskites; c) N_2 physisorption isotherms; HRTEM and EDS analyses of: d) R-$LaNiO_3$-B and e) R-$LaNiO_3$-S; f) Catalytic performance of samples at GHSV = 30 000 mLNH_3/g_{cata}.h

References

1. Züttel, A.; Remhof, A.; Borgschulte, A.; Friedrichs, O. Hydrogen: The future energy carrier. *Philos Trans A Math Phys Eng Sci*. **2010**, 360, 3329–3342.
2. Chatterjee, S.; Parsapur, R. K.; & Huang, K. W. Limitations of Ammonia as a Hydrogen Energy Carrier for the Transportation Sector. *ACS Energy Lett*. **2021**, 6(12), 4390–4394.
3. Chen, C.; Wu, K.; Ren, H.; Zhou, C.; Luo, Y.; Lin, L.; Au, C.; Jiang, L. Ru-Based Catalysts for Ammonia Decomposition: A Mini-Review. *Energy Fuels*. **2021**, 35, 11693–11706

Acknowledgements

The authors thank UE and RW for co-funding the Synfonhy-UCLouvain FEDER project thanks to which the present research was achieved

Alkaline electrolyzer with nanostructured NiFeP electrodes for hydrogen production

Roberto Luigi Oliveri[*,1], Salvatore Geraci[1] , Bernardo Patella[1] , Giuseppe Aiello[1], Sonia Longo[1], Alberto Affranchi[1], Maurizio Cellura[1], Rosalinda Inguanta[1]

[1]*Dipartimento di Ingegneria, Università degli Studi di Palermo, 90128 Palermo, Italy.*

[2] *Centro di Sostenibilità e Transizione Ecologica*

** robertoluigi.oliveri@unipa.it*

Significance and Relevance

This paper presents an innovative Alkaline Water Electrolyser (AWE) based on using NiFeP nanostructured electrodes, from its initial design to its subsequent implementation, as suggested by the results of tests simulating the real-field operation of the electrolyzer. The nanostructured electrodes were fabricated by template electrosynthesis, a straightforward and cost-effective process. This fabrication method was analyzed by Life Cycle Assessment from an eco-design perspective. Electrochemical tests were conducted on the individual electrodes and the complete cell to evaluate their electrocatalytic properties in alkaline solution. The electrodes exhibited robust stability over an extended period (125 hours) with no discernible indications of performance degradation.

Preferred and 2nd choice for the topic: green H2 production, Sustainable and clean energy production
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

In the future, the electrochemical hydrogen production will play an important role. Nevertheless, the cost of electrochemical hydrogen production remains considerably higher than that of conventional production methods. Consequently, research is concentrated on enhancing the functionality of electrolyzers through the utilization of more efficient and cost-effective materials, such as transition metal alloys [1]. For water-alkaline electrolyzers, the development of nanoporous nickel electrodes with low cost and high electrocatalytic efficiency represents a promising strategy for enhancing their performance. A straightforward approach to producing nanostructured electrodes is template electrosynthesis. The methodology employed resulted in the production of electrodes consisting of Ni alloy nanowires with an exceptionally high surface area. The electrodes were produced via a two-step process, resulting in an ordered array of Ni nanowires that completely covered the surface of the current collector, which was also of the same material.

Materials and Methods

NW electrodes were obtained by template electrosynthesis using polycarbonate nanoporous membranes (Whatman). The template has a mean pore diameter of 200 nm and a thickness of about 20 mm. The template electrosynthesis of NW electrodes was performed according to the procedure detailed in [2][3]. Electrodes were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). Each electrode was electrochemically tested, including cyclic voltammetry (CV), quasi-steady state polarization (QSSP), galvanostatic step (GS) and galvanostatic test to evaluate the performance in terms of hydrogen and oxygen production and to verify the medium-term stability under galvanostatic conditions.

Results and Discussion

This study examines the fabrication and characterization of nanostructured nickel alloy electrodes intending to reduce the overpotential losses associated with driving the anodic oxygen evolution reaction (OER) and cathodic hydrogen evolution reaction (HER) in alkaline environments. Ni alloy nanowires (NWs) with an exceptionally high surface area and high electrocatalytic activity were prepared by template electrosynthesis [2]. It was demonstrated that alkaline electrolyzers comprising Ni nanowire electrodes coated with distinct electrocatalysts exhibit robust performance and stability at room temperature [2]. For comparison, functionalized Ni sheets (NS) with the same electrocatalysts were tested. The study of a specific device for alkaline electrolysis was based on the geometry of

devices previously analyzed in the literature and already adapted for use with nanostructured electrodes. A laser cutter was used to define and construct the different components of a cell suitable for containing Ni alloy NWs, Ni alloy NS electrodes, and the diaphragm. An AW laboratory-scale electrolysis system was devised to monitor the operating current and voltage. The comprehensive quantification of these parameters is significant for both fundamental and applied research, as it allows for the determination of the efficiency of an electrochemical device. The electrodes were characterized using SEM and EDS. To assess their performance, QSSP, GS, and galvanostatic tests were conducted over a period exceeding 100 hours at a constant current density. The results presented in this work demonstrate the significant potential of nanostructures to enhance cell performance. The electrodes show excellent long-term stability. With negligible drops in potential, the curve remains almost constant. This alkaline electrolyzer can operate continuously for 125 hours at a current density of 50 with a potential of 1.92 showing an increase of about 3-4 mV after 125 hours. The results presented in this paper show how nanostructures can significantly improve AWE performance. However, further improvements and testing are needed to achieve efficiency levels suitable for industrial use: electrocatalysis can be further improved and the cell design needs to be optimized.

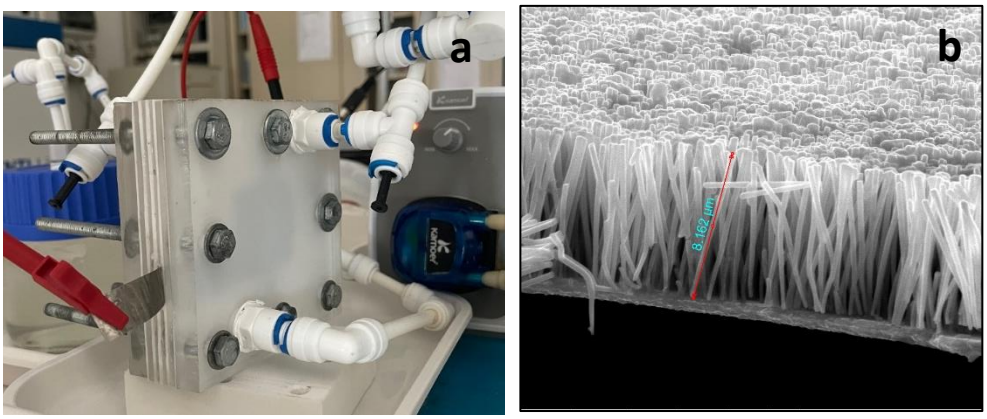


Figure 1. a) The alkaline cell with the NiFeP alloy and b) the SEM of NiFeP alloy NWs used for AWE.

References

1. J. Xu, J. Li, D. Xiong, B. Zhang, Y. Liu, K.-H. Wu, I. Amorim, W. Li, L. Liu, *Chem. Sci.* **2018**, *9*, 3470–3476.
2. Ganci, F.; Cusumano, V.; Livreri, P.; Aiello, G.; Sunseri, C.; Inguanta, R. *Int. J. Hydrogen Energy* **2021**, *46*, 10082–10092.
3. S. Carbone, F. Proietto, F. Bonafede, R. L. Oliveri, B. Patella, F. Ganci, G. Aiello, P. Mandin, M. Kim, M. Scopelliti, R. Inguanta, *Electrochimica Acta* **2023**, *467*, 143120.

Acknowledgements

This work was partially financed by the project "SiciliAn MicronanOTecH Research And Innovation CEnter "SAMOTHRACE" (MUR, PNRR-M4C2, ECS_00000022), spoke 3 - Università degli Studi di Palermo "S2-COMMs - Micro and Nanotechnologies for Smart & Sustainable Communities".

Low-temperature CO_2 methanation over Ni-based catalysts: On the nature of active sites by operando DRIFTS study

Cristina ITALIANO*, Gabriel MARINO, Minju THOMAS, Hafedh BRAHIM, Miriana CAPORLINGUA, Antonio VITA
CNR-ITAE "Nicola Giordano", Via S. Lucia sopra Contesse 5, 98126 Messina, Italy
** cristina.italiano@cnr.it*

Significance and Relevance

CO_2 hydrogenation to methane offers a promising solution for storing excess renewable energy. By using low-cost electricity from intermittent renewable sources, hydrogen is produced through electrolysis and then combined with CO_2 in a catalytic process to create methane. This synthetic methane can be easily stored and transported using existing natural gas infrastructure, providing a stable energy source. Enhancing the efficiency of this process could enable large-scale energy storage, helping to balance supply and demand while reducing carbon emissions.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling; H_2 storage and transportation, green H_2 production, hydrogen vectors
Preferred presentation: Oral preferred or Short Oral / Poster

Introduction and Motivations

The growing atmospheric concentration of carbon dioxide is considered one of the main causes of global warming. Power-to-gas (PtG) processes have the great potential to store the excess of H2 generated from renewable energy, simultaneously reducing CO2 emissions from the atmosphere. In the PtG technology concept, the renewable electricity is used to produce hydrogen by electrolysis of water, and subsequently hydrogen reacts with CO_2 to yield CH_4 via the Sabatier reaction. In this study, we focus on the catalytic behaviors of Ni catalysts supported on Y_2O_3, ZrO_2, CeO_2 and mixed ($YZrO_x$, $CeZrO_x$ and $CeYO_x$) oxides. A comprehensive understanding of the structure-activity correlations was provided to optimally design an effective catalyst for methane production by CO_2 hydrogenation.

Materials and Methods

Ni-based catalysts were synthesized at fixed Ni loading of 25 wt.% by the solution combustion synthesis (SCS) method as literature reported [1-3]. The resulting powder was calcined in static air furnace at 600°C for 2 h. Prior to reaction, the catalysts were in-situ reduced under 50vol.% H_2/N_2 gas mixture (40 $NmL \cdot min^{-1}$) at 600°C for 1 h. The physicochemical properties of the synthesized catalysts were determined by N_2-physisorption, XRD, CO-chemisorption, H_2-TPR, CO_2-TPD, XPS, and TEM. Methanation of CO_2 was investigated under atmospheric pressure, in the temperature range of 250-500°C, at constant stoichiometric reactants ratio of $H_2/CO_2 = 4$ and gas hourly space velocity (GHSV) of 30,000-120,000 $NmL \cdot g^{-1} \cdot h^{-1}$. Furthermore, the formation of intermediates was investigated by in-situ DRIFT tests, to shed light on the mechanism of CO_2 methanation over Ni/CeO_2-ZrO_2 catalyst. A stability test over 100 h of time-on-stream was also performed over the Ni/CeO_2-ZrO_2 catalyst at 250 and 300°C.

Results and Discussion

The main physico-chemical features of all the synthesized catalysts are shown in *Table 1* along with the main reducibility and basicity results. Moreover, Figure 1 displays CH_4 yield for Ni/CeO_2-ZrO_2, Ni/Y_2O_3-ZrO_2 and Ni/ZrO_2 catalysts. In general, the catalytic activity strongly depends on the nature of the Ni-oxide interactions. Based on DRIFT observations, the main reaction pathway involves the adsorption of CO_2 onto catalyst support as mono- or bi-dentate carbonate as well as the H_2 dissociation on metallic Ni sites. The adsorbed CO_2 was progressively hydrogenated to methane passing through the formation of formate species as active intermediate. However, the superior catalytic performance of Ni/CeO_2-ZrO_2 catalyst is mainly due to enhanced medium basicity as well as the relatively high Ni

dispersion, as confirmed by CO_2-TPD and CO-chemisorption measurements. Finally, good anti-coking and anti-sintering ability after 100 h of lifetime test make Ni/CeO_2-ZrO_2 catalyst an effective catalyst to produce methane by CO_2 hydrogenation at low reaction temperatures.

Table 1. Physico-chemical features, reducibility, and basic sites distribution.

Sample	SA_{BET} (m^2/g)	PS_{NiO}[a] (nm)	PS_{Ni}[b] (nm)	Reducibility[c] (%)	Moderate basic sites[d] ($\mu mol_{CO2}/g$)
25Ni/Y_2O_3	20.7	7.5	14.0	88.6	64.2
25Ni/ZrO_2	47.8	8.1	31.9	~100	58.7
25Ni/CeO_2	20.1	15.8	38.9	93.6	1.8
25Ni/20ZrO_2-55Y_2O_3	30.2	6.4	16.4	~100	66.9
25Ni/20CeO_2-55Y_2O_3	14.4	11.5	21.5	94.2	44.3
25Ni/20Y_2O_3-55ZrO_2	70.9	7.6	14.9	~100	75.4
25Ni/20CeO_2-55ZrO_2	54.5	8.3	14.4	~100	122.3

[a]Determined from XRD by the Scherrer's equation of the NiO (111) reflection; [b]Determined by CO-chemisorption; [c]Calculated from H_2-TPR by the ratio between experimental and theoretical H_2 consumption; [d]Calculated from CO_2-TPD between 150 and 450°C.

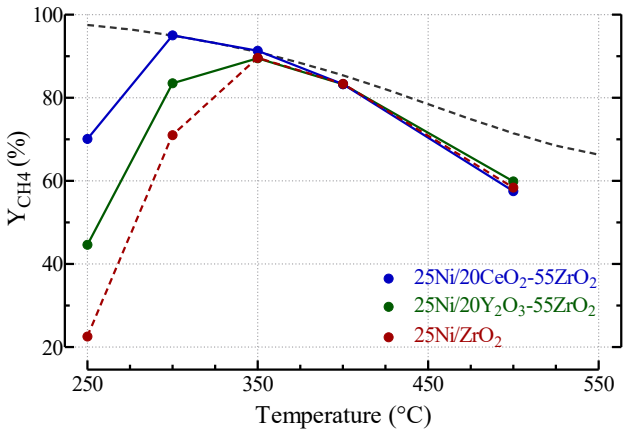


Figure 1. CO_2 methanation activity (*GHSV, 30,000* NmL·g^{-1}·h^{-1}; *$H_2/CO_2/N_2$, 4/1/5*).

References

1. A. Vita et al., Appl. Catal. B 2018, 226, 384
2. C. Italiano et al., Appl. Catal. B 2020, 264, 118494
3. C. Italiano et al., Chem. Eng. J. 2022, 434, 134685

Acknowledgements

This work was partially funded by the Ministry of University and Research (Italy) (MUR), PRIN 2020, within the project "MULTITOOL: CoMbined CO_2 captUre and reduction to methane in compact dual functional reacTors with cellular structured Internals for inTensified heat and mass transpOrt: from labOratory to bench scaLe", Nr. 2020N38E75.
The Research Agreement (POR)-PNRR, "Hydrogen Research - Mission M2-C2 - Investment 3.5: Research and Development on Hydrogen", funded by the Italian Ministry of Ecological Transition (MITE), is particularly acknowledged for funding also part of this work.

Photoreforming of Glycerol for H_2 Production Using Au-Ni Catalysts Supported on CeO_2

Eleonora LA GRECA[1,2*], Roberto FIORENZA[2], Maria Teresa ARMELI IAPICHINO[2] Salvatore SCIRE'[2] and Leonarda Francesca LIOTTA[1]

[1]*Institute for the Study of Nanostructured Materials (ISMN), National Research Council (CNR), Via Ugo La Malfa 153, 90146 Palermo, Italy*

[2]*Department of Chemical Science, University of Catania, Viale A. Doria 6, Catania, Italy Institution, Dept., address, city, country.*

** eleonoralagreca@cnr.it*

Significance and Relevance

The photoreforming of glycerol for hydrogen production offers a sustainable and environmental friendly alternative to the conventional hydrogen generation methods. This process converts glycerol, a renewable by-product of biodiesel production, and water in clean hydrogen fuel [1,2] using solar energy and suitable photocatalysts.

The approach aligns with global energy demands and environmental goals, providing an efficient use of renewable resources.

In this work, the use of Au-Ni photocatalysts supported on CeO_2 enhances the efficiency of hydrogen production addressing also the critical need for cost-effective, stable, and high-performance photocatalysts in renewable energy applications.[3–5]

Preferred and 2nd choice for the topic: (1) H_2 storage and transportation, green H_2 production,hydrogen vectors; (2) Photocatalysis and photoelectrocatalytic approaches, solar energy utilization

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The transition toward renewable energy sources has driven extensive research into alternative methods for hydrogen production, with photocatalytic reforming emerging as a promising technology.[6,7] Glycerol, abundantly produced as a by-product in the biodiesel industry, can be used as potential feedstock for this process. The key to maximize hydrogen yields lies in the development of efficient photocatalysts. In this study we explore bimetallic Au-Ni catalysts supported on cerium oxide due to their unique properties: CeO_2 provides high oxygen storage capacity and stability, while the Au-Ni alloy exhibits enhanced catalytic properties. Nickel facilitates the oxidation of glycerol, while gold improves electron transfer, resulting in higher hydrogen yields and improved catalyst stability. This work aims to advance the understanding and the application of Au-Ni/CeO_2 catalysts in the solar photoreforming, promoting their use as a sustainable solution for hydrogen generation.

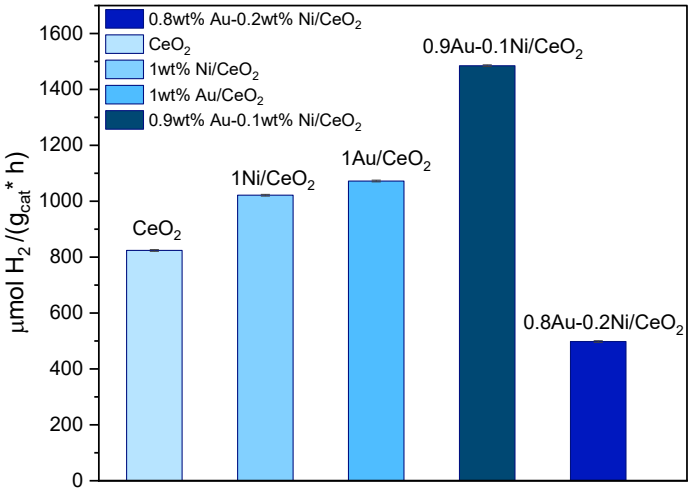
Materials and Methods

CeO_2 was prepared by precipitation in basic conditions starting from $Ce(NO_3)_3{\cdot}6H_2O$, the resulting precipitate was hydrothermally aged at 120 °C and calcined at 600 °C. Ni was deposited on ceria by wetness impregnation method, using $Ni(NO_3)_6{\cdot}H_2O$, whereas gold was supported on ceria via deposition-precipitation method, by using a solution of $HAuCl_4$. For the bimetallic Au-Ni catalysts, Au was deposited as first, then, Ni was added. All the prepared catalysts were calcined at 250 °C. The metal composition was 0.9wt% Au-0.1wt% Ni/CeO_2 and 0.8wt% Au-0.2wt% Ni/CeO_2 for the bimetallic catalysts, 1wt% of Au or Ni for the monometallic ones.

The photocatalytic hydrogen production was conducted under solar irradiation, with a suspension of 1 mg mL^{-1} of catalyst in 10% (v/v) solution of glycerol in MilliQ water. The solar irradiation was performed with a special lamp specifically designed for the sunlight simulation. After 5 h of irradiation, 1 mL of reaction gases was collected with a gastight syringe and analysed by gas chromatography with a thermal conductivity detector (GC-TCD).

Results and Discussion

The catalytic activity of Au, Ni and Au-Ni catalysts supported on CeO_2 provided valuable insights into their efficacy in the H_2 production. Bare ceria and all the supported catalysts demonstrated significant H_2 photoreforming activity (Fig.1), with 0.9wt% Au-0.1wt% Ni/CeO_2 that showed heightened efficiency, suggesting an important synergistic effect between Au and Ni. In comparison with ceria alone, the addition of Ni improves the hydrogen production activity, likely enhancing the cleavage of C–C and C–H bonds of glycerol thanks to the high work function of such metal promoting efficient electron transfer and glycerol photoreforming activity.[5] Gold plasmonic resonance amplifies light absorption and enables greater visible light utilization, moreover, it is expected to prevent Ni agglomeration.[8] The interaction between Au and Ni metals appears particularly pronounced in the catalyst with composition 0.9wt%Au-0.1wt%Ni/CeO_2, whereas the activity is depleted in the 0.8wt%Au-0.2wt%Ni/CeO_2. Characterizations of the structural, morphological, electronic and reduction properties were carried out in order to explain the reasons that promote a such effective synergy between the two metals, in correspondence of this specific Au-Ni composition, optimizing their performance in the photocatalytic applications.



References

1. A. V. Puga, *Coord. Chem. Rev.* **2016**, *315*, 1–66.
2. J.G. Villachica-Llamosas; J. Sowik; A. Ruiz-Aguirre; G. Colón; J. Peral; S. J. Malato. *Environ. Chem. Eng.* **2023**, *11*, 0–7.
3. S.A. Balsamo; E. La Greca; M. Calà Pizzapilo; S. Sciré; R. Fiorenza. *Materials.* **2023**, *16*, 1–13.
4. R. Fiorenza; S.A. Balsamo; M. Condorelli; L. D'Urso; G. Compagnini; S. Scirè. *Catal. Today* **2021**, *380*, 187–198.
5. J. Zhang; Y. Zhu; Z. An; X. Shu; X. Ma; H. Song; W. Wang; J. *ACS Appl. Energy Mater.* **2020**, *3*, 7048–7057.
6. X. Xu; Q. Zhou; D. Yu. *Int. J. Hydrogen Energy* **2022**, *47*, 33677–33698.
7. P. Nikolaidis; A. Poullikkas. *Renew. Sustain. Energy Rev.* **2017**, *67*, 597–611.
8. H. Zhao; P. Liu; X. Wu; A. Wang; D. Zheng; S. Wang; Z. Chen; S. Larter; Y. Li; B.L. Su; et al. *Appl. Catal. B Environ.* **2021**, *291*.

Acknowledgements

Eleonora La Greca thanks the University of Perugia for the National PhD scholarship in catalysis.

Detection of Hydroxylamine Intermediate Opens a New Perspective on Ammonia Selectivity in Metal-Catalyzed Nitrate Reduction

Janek BETTING*[,1], Leon LEFFERTS[1], Jimmy FARIA ALBANESE[1]
[1]*University of Twente, Faculty of Science and Technology, Drienerlolaan 5, 7522NB Enschede, The Netherlands.*
**j.betting@utwente.nl*

Significance and Relevance

In the catalytic reduction of nitrates in drinking water, undesired NH_4^+ formation is the main drawback yet hindering this technology from industrial application. Despite that most studies claim nitrites (NO_2^-), ammonium cations (NH_4^+), and nitrogen (N_2) as the exclusive reaction products, we found hydroxylamine (NH_2OH) as additional product under typical NO_3^- reduction conditions (~pH 6). We observed the degradation of NH_2OH into NH_4^+ over time suggesting that NH_2OH may be formed in typical NO_3^- reduction systems, but might be overseen if not specifically searched for. This observation questions not only NH_4^+ selectivity in existing studies, but also gives a new perspective on the underlaying reaction mechanism of the catalytic NO_3^- reduction.

Introduction and Motivations

In the European Union around 14 % of the groundwater stations exceeded the NO_3^- limit of 50 mg/L, and about one third of the land waters and more than 80 % of the ocean waters in the EU are considered eutrophic, showing the demand for improved NO_3^- management.[1] Catalytic NO_3^- reduction is a potential technology to remove NO_3^- from water bodies by actually degrading it into harmless N_2, which makes it in this aspect superior to alternative techniques such as reverse osmosis, ion exchange or electrodialysis as no concentrated waste brines are generated.[2] Bimetallic Pd-Cu, Pd-Sn and Pd-In catalysts actively reduce NO_3^- in the presence of H_2 at RT and atmospheric pressure while the major challenge is the undesired NH_4^+ production as e.g. the limits in drinking water are even stricter than for NO_3^- (0.5 mg/L vs. 50 mg/L).[2]

The standard procedure in scientific literature is to determine NH_4^+, NO_2^- and NO_3^- concentrations by IC or HPLC, assuming that the remainder is N_2. Closing the N mass balance entirely is extremely challenging as gas and liquid phase samples exhibit a delay but must be matched. Additionally, contamination with atmospheric N_2 is difficult to suppress. Only few studies achieve a closed mass balance over parts of the reaction time,[4] or during the entire reaction only by using isotope labeled N.[3] In this study, we show an easy method to detect NH_2OH in NO_3^- reduction as it is easily overseen if not carefully checked for.

Materials and Methods

A Pd/Al_2O_3 catalyst (2.5 wt% Pd, 181 m^2/g, < 45 µm) was prepared via Strong Electrostatic Adsorption method ($[Pd(NH_4)_4](NO_3)_2$ and $NH_{3,aq}$). From this, a bimetallic $SnPd/Al_2O_3$ (Pd : Sn ratio 1.4 : 1) catalyst was prepared via sequential impregnation ($SnCl_2$ in ethanol). The catalysts were characterized by XRF, CO-chemisorption, N_2-physisorption, XRD and TEM. NO_3^- and NO_2^- (1 mM) were converted in a 1 L semi-batch reactor under continuous gas flow (H_2, CO_2, He) in the absence of mass transport limitations. Liquid samples were taken over time and benzaldehyde or acetone were added to derivatize NH_2OH into the corresponding oxime. NO_3^-, NO_2^- and NH_4^+ were quantified by ion chromatography and the oxime by HPLC or GC after derivatization.

Results and Discussion

In a conventional NO_3^- reduction experiment over a $SnPd/Al_2O_3$ catalyst, NO_2^- is only observed in traces (≤0.01 mM) and the NH_4^+ concentration increases with increasing NO_3^- conversion but plateaus after full NO_3^- depletion. However, we observed increasing NH_4^+ concentrations even after full NO_3^-

conversion. Therein, the NH_4^+ concentration increase was larger than the accessible moles of metal surface and could thus not be explained by desorption of surface N-species suggesting an additional reaction intermediate, which could be defined as NH_2OH by it trapping into an oxime with benzaldehyde or acetone (Figure 1 **B**).

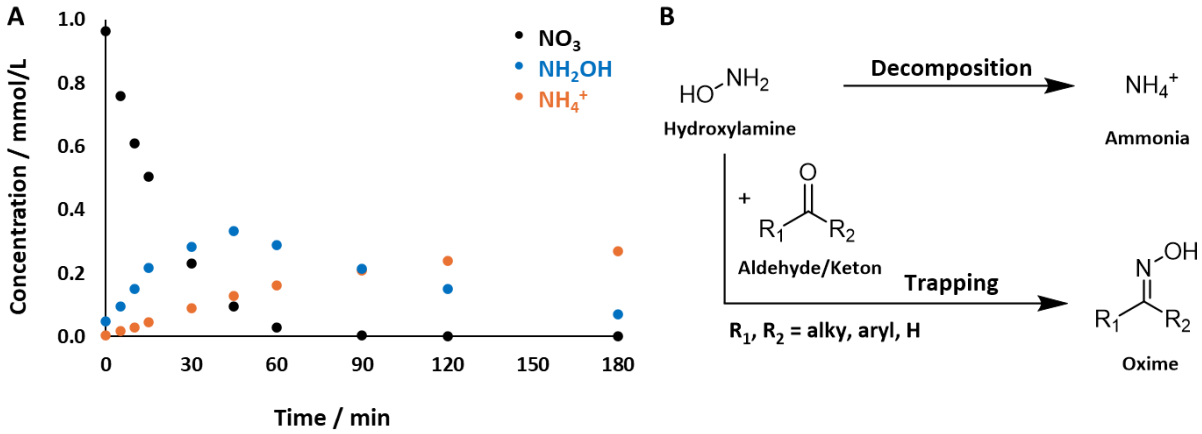


Figure 1: A Concentration profile of NO_3^- reduction reaction. Reaction conditions: 1 mM KNO_3, 50 mg $SnPd/Al_2O_3$, 80:10:10 mL/min H_2:CO_2:He, RT, 300 mL milli-Q water, 600 rpm. **B** Schematic reaction pathway of NH_2OH trapping into an oxime or decomposition into NH_4^+.

The typical concentration profile in Figure 1 **A** shows an initially strong NH_2OH formation resulting in a maximum NH_2OH selectivity of 47 %. Over time, NH_2OH decomposes mainly into NH_4^+, but as the sum of NH_2OH and NH_4^+ concentration decreases, also partly into N_2. The NH_2OH decomposition occurs also after catalyst removal and is thus non-catalytic. Experiments to elucidate whether the decomposition follows a hydrogenation or disproportionation are ongoing.

The addition of hydroxylamine scavenger in the reactor does not entirely suppress the NH_4^+ formation indicating that probably not all NH_4^+ is formed via the NH_2OH pathway or, less likely, the difference in oxime formation rate and NH_2OH decomposition rate is insufficiently large to trap all NH_2OH. These research questions are currently under investigation in our group also for the NO_2^- reduction on $SnPd/Al_2O_3$ and Pd/Al_2O_3 catalysts.

This study suggests that NH_2OH is possibly a key reaction intermediate in the NO_3^- reduction reaction over a $SnPd/Al_2O_3$ catalyst. Trapping this NH_2OH using acetone or benzaldehyde into an oxime offers a simple and transferrable quantification strategy, which can substantially improve our understanding of this reaction. The detection of NH_2OH as reaction intermediate should encourage to critically question reported NH_4^+ selectivity and more broadly the reaction mechanism behind NH_4^+ and N_2 formation.

References

1. European Commission, Report on the implementation of Council Directive 91/676/EES concerning the protection of waters against pollution caused by nitrates [...] **2021**.
2. I. Sanchis, E. Diaz, A.H. Pizarro, J.J. Rodriguez, A.F. Mohedano, *Sep. Purif. Technol.* **2022**, 290, 120750.
3. R. Zhang, D. Shuai, K. A. Guy, J.R. Shapley, T.J. Strathmann, C.J. Werth, ChemCatChem **2013**, 5, 313-321.
4. U. Prüsse, J. Daum, C. Bock, K.-D. Vorlop, Stud. Surf. Sci. **2000**, 130, 2237-2242.

Acknowledgements

We acknowledge the financial support provided through grant number 20002675 LNG-Zero project.

Catalytic hydrogenation of chlorated oxyanions in water with Pt-catalysts

Antonio .Eduardo Palomares[1], Adrián Pla-Hernández[1], Nadia Benmebirouk-Pareja[1]
[1]*Instituto de Tecnología Química (Universidad Politécnica de Valencia - Consejo Superior Investigaciones Científicas), 46022 Valencia, Spain*
**apalomar@iqn.upv.es*

Significance and Relevance

Catalytic hydrogenation is used to remove chlorate ions from water streams at room temperature and atmospheric pressure by using supported platinum catalysts. The catalysts have been supported on different materials as γ-Al_2O_3 and TiO_2 and a second transition metal (vanadium) has been added in order to improve the reaction rate. The catalytic studies showed an important influence on the support, being the catalysts supported on TiO_2 the most actives indicating that the photochemical and acid properties of this material enhances the catalytic activity of the platinum centers. The main novelty of these results is that the catalyst has been tested in natural polluted water obtaining interesting results.

Preferred for the topic: Water treatment
Preferred presentation: *Oral only*

Introduction and Motivations

Water is an essential resource for life and it is necessary to ensure its quality, mainly when it is used for human consumption. An emerging pollutant that may be present in water is the chlorate ion that could be generated during the disinfection treatment of natural water using oxidizing agents, such as chlorine dioxide or ozone. Chlorates are harmful to health, as they can oxidize haemoglobin, leading to haemolytic anaemia. Additionally, some research has shown that chlorates can interfere with iodine uptake by the thyroid gland and negatively impact both the quantity and quality of sperm. Due to these health risks, the World Health Organization (WHO) has set a provisional limit of 0.7 mg/L for chlorates in drinking water[1].

As a result of this, there is a necessity of sustainable methods able to remove this pollutant from natural water. Catalytic hydrogenation has been suggested as a potential solution for treating this pollutant as it can be reduced to innocuous chloride according to:

$$ClO_3^- + H_2 \rightarrow Cl^- + H_2O$$

Van Santen et al[2]. patented a method to remove chlorate from solutions using monometallic catalysts based on noble metals supported on SiC, ZrO_2, Al_2O_3, activated carbon and graphite, among others. The results of this patent establish the following sequence of activity against chlorate reduction: Rh > Pt > Pd. Despite these results, most studies have focused mainly on catalysts based on Pd supported on different carbonaceous materials. Ren et al.[3] used Pd/C catalysts with immobilised MoO_x as a promoter for chlorate reduction. They found that at pH = 3, the MoO_x-Pd/C catalysts showed activity comparable to the activity of monometallic Rh. Another way to improve the catalytic activity is by using vanadium promoters dissolved in water. Gao et al[4]. have used Pd/C composite catalysts together with a vanadium promoter dissolved in water for the reduction of ClO_3^-.

Hereby, we continue our previous study with monometallic materials[5], studying the performance of different bimetallic Pt-V catalysts supported on different oxides for the hydrogenation of chlorate at room temperature and atmospheric pressure.

Materials and Methods

The catalysts were prepared by incipient wetness impregnation of Al_2O_3 and TiO_2 in order to have catalysts with different Pt/V ratios. The support was initially impregnated with a solution of $VOSO_4$, dried and calcined at 773 K. After that, a solution of $PtCl_4$ was added and the catalyst was dried and calcined again at 623K. The catalysts were reduced with hydrogen at 473 K for 4 h before the reaction. The experiments were made in a batch-stirred tank reactor at room temperature and atmospheric pressure, using hydrogen as a reducing agent. The typical experiments used 1 g of catalyst and 0,6 L of water with 50 ppm of chlorates. The analysis of the reactants and products was made by ionic chromatography. The catalysts were characterised through different techniques such as ICP, XRD, TPR, N_2 adsorption and IR and UV spectroscopies.

Results and Discussion

The catalytic studies were made using mono and bimetallic catalysts with different Pt:V ratios. As it can be seen in Figure 1 left the bimetallic catalyst supported on Al_2O_3 has a significant increase of the activity compared to the monometallic ones indicating a synergic effect of Pt and V that results in an important increase of the catalyst activity. The influence of the support was studied by comparing the results obtained with catalysts supported on Al_2O_3 with those with the same composition but supported on TiO_2. It is again observed that the bimetallic catalyst is more active than Pt-monometallic catalysts, whilst V-catalyst is not active. Nevertheless, catalysts supported on TiO_2 are much more active than those supported on Al_2O_3. As can be seen in Figure 1 right, the 5%Pt/TiO_2 catalyst reduces 80% of chlorate in 15 minutes and the 5%Pt-5%V/TiO_2 bimetallic catalyst achieves the same conversion in 2.5 minutes. It was also observed that catalyst activity decreases in darkness, indicating that together with the hydrogenation, a photocatalytic reaction is occurring. The combination of the photocatalytic properties of titania, its acidic properties and the synergic effect of Pt-V metals results in the high activity obtained with this catalyst for the chlorate reduction. This catalyst has been used in natural polluted water and in these conditions, the reaction rate decreases probably because there is a competitive adsorption of the other ions present in natural water on the active sites. Even that, the catalyst is active indicating that Pt/V bimetallic catalysts are active in the removal of chlorates in aqueous phase using H_2 as a reduction agent.

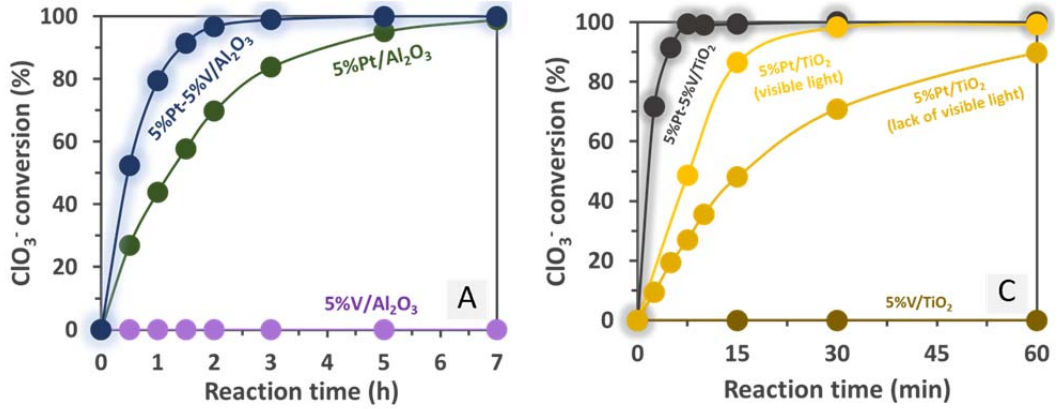


Figure 1 Conversion of Pt-catalysts supported on alumina and titania for the catalytic reduction of chlorates.

References

1. Guidelines for drinking-water quality: 4th edition, World Health Organization, Geneva **2022**.
2. G. Rutger Van Santen, L. Armin Klesing, E. Gerhard Neuenfeldt, H. Alfred Ottmann, U.S. Patent No 6,270,682, **2001**.
3. C. Ren, P. Yang, J. Gao, X. Huo, X. Min, E. Y. Bi, Y. Liu, Y. Wang, M. Zhu, J. Liu, ACS Catal. **2020,** 10 8201-8211.
4. J. Liu and J. Gao, Frontiers of Environmental Science & Engineering, **2023,** 17, 26.
5. A. Plá-Hernández, F. Rey and A.E. Palomares, Catalysis Today **2024,** 429, 114461.

Catalytic ozonation of pharmaceutical mixtures: A comprehensive analysis of catalyst efficacy, degradation pathways and recyclability

Pasi TOLVANEN*[1], Soudabeh SAEID[1], Matilda KRÅKSTRÖM[1], Shey JUDE FALE[1,3], Nikke SAARINEN[1], Jonna ENGSTRÖM-ÖST[3], Narendra KUMAR, Patrik EKLUND[1], Jyri-Pekka MIKKOLA[1], Tapio SALMI[1,2]

[1]Åbo Akademi, Johan Gadolin Process Chemistry Centre (PCC), FI-20500 Turku/Åbo, Finland
[2]Università di Napoli 'Federico II', Chemical Sciences, IT-80125 Napoli, Italy
3 Novia University of Applied Sciences, FI-10650, Finland
**pasi.tolvanen@abo.fi*

Significance and Relevance

This study explores catalytic ozonation as a promising approach for the degradation of pharmaceutical contaminants in wastewaters. Leveraging our previous work on single pharmaceuticals, such as ibuprofen, diclofenac, carbamazepine, and sulfadiazine, this work is focused on the effectiveness of various heterogeneous catalysts in degrading complex pharmaceutical mixtures. The findings include degradation efficiencies, key degradation products, and the structural stability of catalysts, potentially advancing catalytic ozonation as a viable solution for environmentally sustainable water treatment.

Preferred choice for topic: Water treatment; Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Pharmaceutical residues in wastewaters present a persistent environmental threat, since they accumulate in aquatic environments, especially in sensitive regions such as the Baltic Sea where concentrations can persist for decades[1]. In our previous studies we have demonstrated that combined ozonation and heterogeneous catalysis can successfully degrade individual pharmaceuticals, such as ibuprofen, diclofenac, carbamazepine, and sulfadiazine[2-5]. In Figure 1, these pharmaceuticals along with their main transformation products are depicted. In general, the decomposition proceeds in two stages: ozone creates radicals which initiate the decomposition, and the primary decomposition products are degraded by heterogeneous catalysts[2-5]. However, in real wastewaters, pharmaceuticals appear as complex mixtures. Therefore, our current research is focused on the investigation of mixtures of pharmaceuticals. Important synergistic and antagonistic effects will be carefully monitored when these multiple compounds as well as their break-down components interact, to ensure that the treated mixture becomes less toxic than before the treatment. Effective and inexpensive catalysts are explored, focusing on iron- and copper-based materials, with the aim of scalability and economic feasibility for industrial applications.

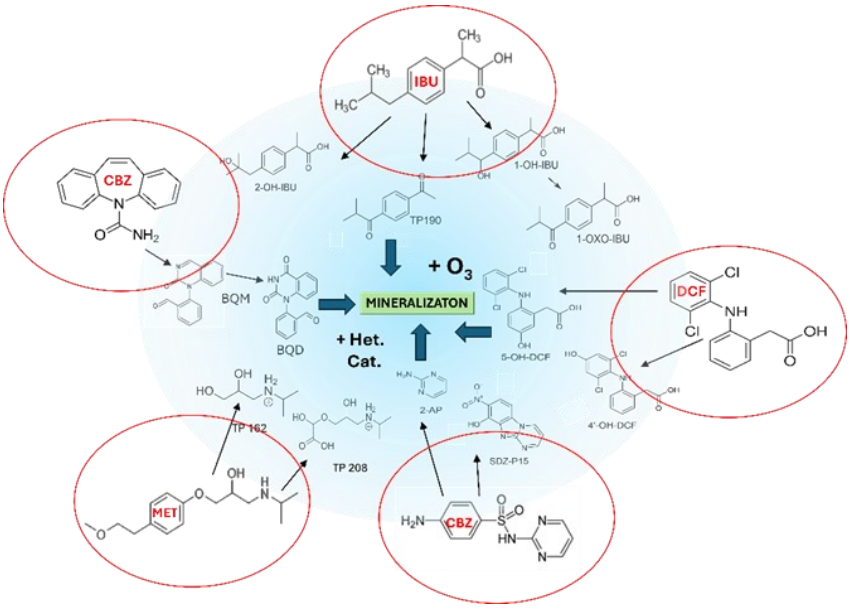


Figure 1. Primary transformation products identified from the ozonation of the five pharmaceuticals studied. These compounds feature a variety of reactive functional groups, including amines and quinones, which can facilitate further breakdown through additional reactions, ultimately aiding in the progression toward complete mineralization.

Materials and Methods

The study employs batch and continuous ozonation reactors to screen a range of heterogeneous catalysts, including transition metal oxides and modified carbon materials. Characterization techniques, such as nitrogen physisorption, SEM, and XRD, were used to monitor the changes of the material properties before and after the catalytic ozonation experiments. Pharmaceutical mixtures representative of five common highly detected contaminants in wastewater are prepared, and HPLC and MS are utilized to track the degradation intermediates and identify degradation pathways. Key degradation products, including potentially toxic intermediates such as quinones, are identified to provide insights into the reaction mechanisms and minimize the amounts of harmful by-products.

Results and Discussion

Initial findings from catalytic ozonation experiments on single pharmaceuticals reveal significant differences in the degradation efficiency depending on the catalyst. For instance, previous research has shown that Pt-modified catalysts enhance ozonation efficiency for diclofenac, yielding higher degradation rates and reducing the amount of toxic by-products[2]. On the other hand, the toxic intermediates BQD and BQM arising from ozonation of carbamapezine were closely monitored, since they are known for their persistency. The best catalyst for eliminating these compounds have found to be Pd-H-Y-12-EIM, but Pd is an expensive metal. Therefore, Fe and Cu based catalysts are screened here, due to their cost-effectiveness and high activity in generating reactive oxygen species (ROS), which drive the degradation process. Preliminary hypotheses suggest that catalysts promoting ozone decomposition enhance the production of hydroxyl radicals, accelerating the degradation process. Attention is also given to the formation of harmful by-products and the catalyst durability studies. Therefore, the spent catalysts are analyzed to provide insights into catalyst life time.

References

1. B. Björnelius, M. Ripszám, P. Haglund, R. Lindberg, M. Tysklind, J. Fick, Pharmaceutical residues are widespread in Baltic Sea coastal and offshore waters – Screening for pharmaceuticals and modelling of environmental concentrations of carbamazepine, *Science of the Total Environment* **2018**, 633, 1496-1509.
2. S. Saeid, B. P. Tolvanen, N. Kumar, K. Eränen, J. Peltonen, M. Peurla, J-P. Mikkola, A. Franz, T. Salmi, Advanced oxidation process for the removal of ibuprofen from aqueous solution: a non-catalytic and catalytic ozonation study in a semi-batch reactor, *Applied Catalysis B: Environmental* **2018**, 230, 77–90.
3. M. Kråkström, S. Saeid, P. Tolvanen, N. Kumar, T. Salmi, L. Kronberg, P. Eklund, Identification and Quantification of Transformation Products Formed during the Ozonation of the Non-steroidal Anti-inflammatory Pharmaceuticals Ibuprofen and Diclofenac, *Ozone: Science and Engineering* **2021**, 44(2), 157-171.
4. M. Kråkström, S. Saeid, P. Tolvanen, T. Salmi. P. Eklund, L. Kronberg, Catalytic ozonation of the antibiotic sulfadiazine*, Chemosphere* **2020**, 247, 125853.
5. S. Saeid, M. Kråkström, P. Tolvanen, N. Kumar, K. Eränen, J-P. Mikkola, L. Kronberg, P. Eklund, M. Peurla, A. Aho, A. Shchukarev, T. Salmi, Advanced oxidation process for degradation of carbamazepine from aqueous solution: influence of metal modified microporous, mesoporous catalysts on the ozonation process, *Catalysts* **2020**, 10, 90.

Acknowledgements

Financial support from Lieto Savings Bank Foundation is gratefully acknowledged.

Keggin heteropolyanions: novel versatile deoxydehydration catalysts

Alixandre MAGERAT*, Sophie HERMANS, Eric M. GAIGNEAUX
Université catholique de Louvain (UCLouvain), Institute of Condensed Matter and Nanosciences (IMCN), Place Louis Pasteur, 1 – 1438 Louvain-la-Neuve, Belgium
**alixandre.magerat@uclouvain.be*

Significance and Relevance

Deoxydehydration (DODH) is an important reaction to upgrade (bio-based) polyols and make them practically useful[1]. Catalysts for this transformation are generally Mo, Re or V-based organometallics or oxides[2], while the use of Keggin heteropolyanions (HPAs) has never been reported before. We report here, for the first time, the promising catalytic performance of $(TBA)_3PMo_{12}O_{40}$ (TBA = tetrabutylammonium), a simple HPA obtained by precipitation of the commercially available $H_3PMo_{12}O_{40}$ with TBA^+. Additionally, we show that substituting a W by Re in $PW_{12}O_{40}^{3-}$ dramatically increases its DODH-activity, hence demonstrating the high versatility of HPAs. Characterizations (IR, ^{31}P NMR and UV-vis) of the used catalysts are provided to investigate the nature of the active species of these novel catalysts.

Preferred and 2nd choice for the topic: "Green Chemistry and biomass transformation, renewable resources conversion"
Preferred presentation: Oral only

Introduction and Motivations

Most of today's chemicals production relies on fossil fuels, but their finite nature requires exploring alternative raw material sources. The use of biomass-derived compounds as such is a promising yet challenging option due to their polyoxygenated nature, often under the form of polyhydroxylated chains. Such functionality (vicinal diols) can be transformed into readily functionalizable alkene through DODH (Fig. 1). Hereunder, we describe a pioneering work where Keggin HPAs are used as DODH catalysts for the very first time.

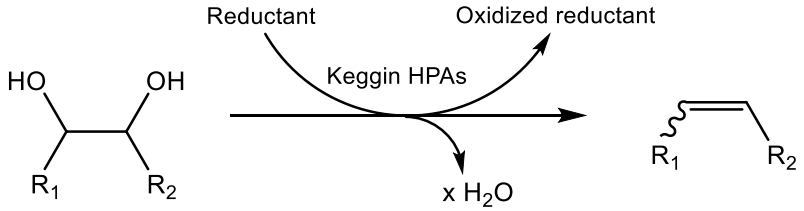


Figure 1. Deoxydehydration reaction. The number of H_2O molecules produced depends on the reductant's nature.

Results and Discussion

Keggin phosphomolybdates and -tungstates ($PM_{12}O_{40}^{3-}$ = PM with M being Mo or W) were first considered as potential catalysts and tested in the model DODH of 1,2-hexanediol into 1-hexene (reaction on Fig. 2 (b)). Three different counter-cations were considered, namely H^+ (HPM), NH_4^+ (NH_4PM) and tetrabutylammonium (TBAPM) (Fig. 2 (a)). Within both W and Mo series, TBAPMs showed the highest 1-hexene yields. This was attributed to the absence of Bronsted acidity as the latter is known to be undesired for DODH catalysis, hence explaining the lower yields obtained with HPMs and NH_4PMs.

Additionally, PW demonstrated lower-DODH activity than their PMo counterparts, likely because W has less redox flexibility than Mo. To improve the DODH activity of TBAPW, we consented to a synthetic effort to replace one of the 12 tungsten atoms in the PW anion by a rhenium(V) one, yielding $(TBA)_4PW_{11}Re^VO_{40}$ ($TBAPW_{11}Re$). The latter was fully characterized by ^{31}P NMR, IR (Fig. 2 (d-f)), ICP-AES,

PXRD and UV-vis (not shown here). The obtained 1-hexene yield was greatly improved with TBAPW$_{11}$Re, increasing from 9% for TBAPW to 73% for TBAPW$_{11}$Re (Fig. 2 (b)).
Recyclability tests (Fig. 3 (c)), combined with IR and ^{31}P NMR analyses (Fig. 3 (d-f)), revealed that TBAPMo and TBAPW$_{11}$Re undergo partial, non-destructive dissolution during catalytic tests. Indeed, TBAPW$_{11}$Re showed the same IR and ^{31}P NMR spectrum before and after catalysis.

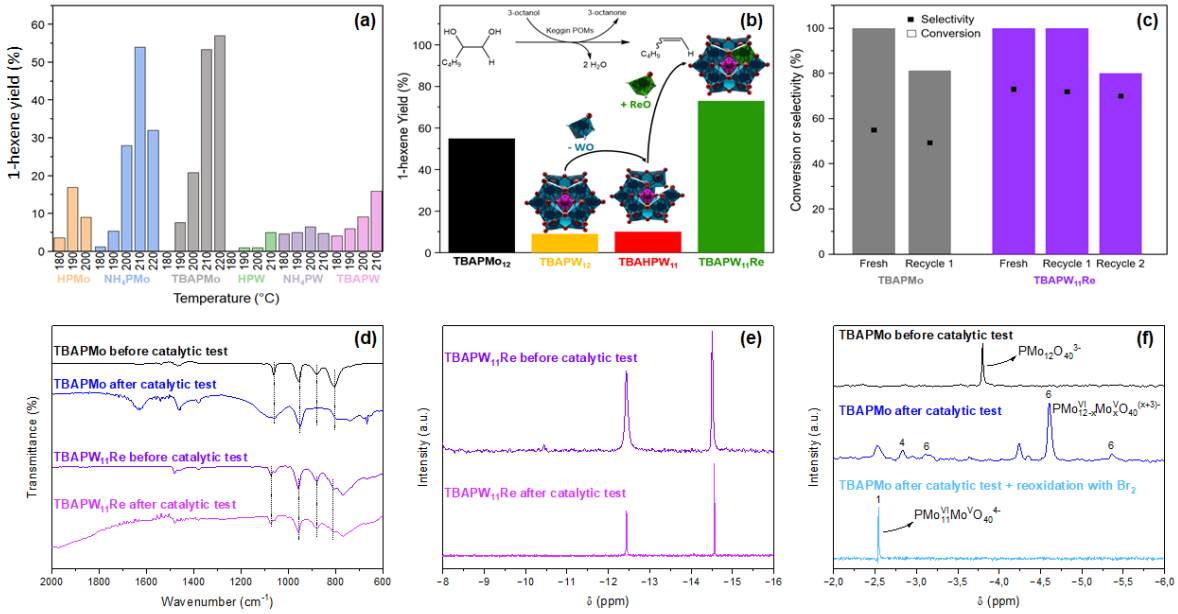


Figure 2. Catalytic performances of (a) HPMs, NH_4PMs and TBAPMs (M=Mo or W) at different temperatures and (b) TBAPMo, TBAPW, TBAHPW$_{11}$ (monolacunary form of TBAPW, $(TBA)_4H_3PW_{11}O_{39}$) and TBAPW$_{11}$Re at 210°C. Reaction conditions: 18h; 5 mL of 1,2-hexanediol (0.1 mol/L) with n-dodecane as internal standard (0.1 mol/L); 5% Mo or W mol. or 2% mol Re. (c) Recycling experiments with TBAPMo and TBAPW$_{11}$Re. (d) IR and ^{31}P NMR (e-f) spectra of TBAPMo and TBAPW$_{11}$Re before and after catalytic tests.

After catalysis, TBAPMo presented several peaks in ^{31}P NMR that are attributed to several $(TBA)_3PMo^{VI}_{12-x}Mo^{V}_{x}{}^{x-}$ species. The one-electron reduced TBAPMo could be obtained when it was reacted with Br_2, showing the reversibility of this reduced state. TBAPMo after catalytic test presented the same IR spectrum as before, at the exception of broadened Mo-O-Mo bands with decreased intensity. This behaviour has already been reported and is due to a strong coupling of bipolaron with the vibration of the bridging Mo-O-Mo bonds[3]. Hence, these results are also in line with a preserved Keggin structure.

Conclusion

This work represents the pioneering use of Keggin polyoxometalates as a versatile platform for the elaboration of performant deoxydehydration catalysts and is laying the groundwork for future catalytic systems including Keggin POMs for biomass valorization processes. Future works will entail exploring new POM formulations and optimizing their recovery and reuse.

Acknowledgements

The Université catholique de Louvain (UCLouvain) is acknowledged for the teaching assistant position.

References

1. F.C. Jentoft, *Catal. Sci. Technol.* **2022**, *12*, 6308-6358.
2. N.N. Tshibalonza, J.C.M. Monbaliu, *Green Chem.* **2017**, *19*, 3006-3013.
3. M. Fournier, C. Rocchiccioli-Deltcheff, L.P. Kazansky, *Chem. Phys. Lett.* **1994**, *4*, 297-300.

Enhanced Bio-Oil Upgrading: Mesoporous and Zeolitic Catalysts for Polyaromatic Hydrocarbon Conversion

Luke HARVEY, Thoams DOYLE, Rahim KAMARI, Eric KENNEDY, Michael STOCKENHUBER
The University of Newcastle, Chemical Engineering, University Drive, Callaghan, Australia
**Luke.Harvey@newcastle.edu.au*

Significance and Relevance

The sustainable transformation of biomass-derived bio-oils into fuels and platform chemicals is central to reducing reliance on fossil hydrocarbons. This work addresses a critical limitation in bio-oil upgrading: the efficient conversion of bulky polycyclic aromatic hydrocarbons (PAHs), which constitute a major fraction of bio-oil carbon, into valuable products. We present the synthesis and application of mesoporous catalysts tailored to enhance PAH conversion, coupled with zeolitic materials for selective cracking, offering a promising pathway for advanced biomass valorization.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion
Preferred presentation: *Oral only*

Introduction and Motivations

Global energy security increasingly relies on sustainable alternatives to crude oil derivatives and hydrocarbons. This research advances catalytic technologies to convert biocrude, derived from waste and biomass sources (e.g., lignocellulose), into fuels and high-value platform chemicals. A primary challenge in bio-oil upgrading is reducing oxygen content, which impacts stability and usability[1]. Recent studies show that zeolite-based catalysts are highly effective in hydrodeoxygenation, offering control over selectivity for products such as BTEX, through structural and acidic site modifications[2]. The micropores found in most common zeolitic materials, however are not easily accessible to bulkier compounds (PAHs) which comprise a high proportion of the carbon in bio oils. It is therefore preferable to select mesoporous catalyst supports. By optimizing catalyst properties including acid site strength and concentration, pore size and structure and catalytic metal loading, we have shown that PAH conversion is significantly increased, and selectivity may be directed toward either hydrogenated kerosene products, or single-ring aromatics and derivatives.

Materials and Methods

The mesoporous support was synthesized by mixing the required amounts of aluminum isopropoxide and tetraethyl orthosilicate together with P123 as a structure directing agent under acidic conditions. The resulting gel was aged in a PTFE-lined autoclave at 110°C for 48 hours. Aluminium-free mesoporous silica was prepared using the same method but omitting the aluminum source. Loading of the nickel was performed by wetness impregnation, followed calcination at 500°C.
Catalyst textural properties were measured using nitrogen sorption at liquid nitrogen temperature. Acid site strength and concentration was measured using ammonia temperature-programmed desorption (TPD) with a mass spectrometer.
The reaction was carried out in a vertical fixed bed plug flow reactor at elevated hydrogen pressure. A simulated bio-oil feed containing phenanthrene as a surrogate for the three-member polyaromatic hydrocarbons which constitute the largest and most challenging family of compounds comprising bio-oil, dissolved in 3-pentanone was introduced using a high pressure syringe pump.
Feed and product streams were analyzed by gas chromatography, using MSD, FID, TCD and methanizer-FID detectors.

Results and Discussion

Catalyst Characterization: The pore size distribution of the mesoporous aluminosilicate was relatively narrow and centered on
79 Å, slightly larger than the aluminum-free SBA-15 at 66 Å. The addition of nickel reduced the effective pore diameter of the Al-ABA-15 and SBA-15 by approximately 10 Å. This was not the case for zeolite BEA, with H-BEA and Ni-H-BEA having pore diameters of 7.1 and 7.0 Å respectively.

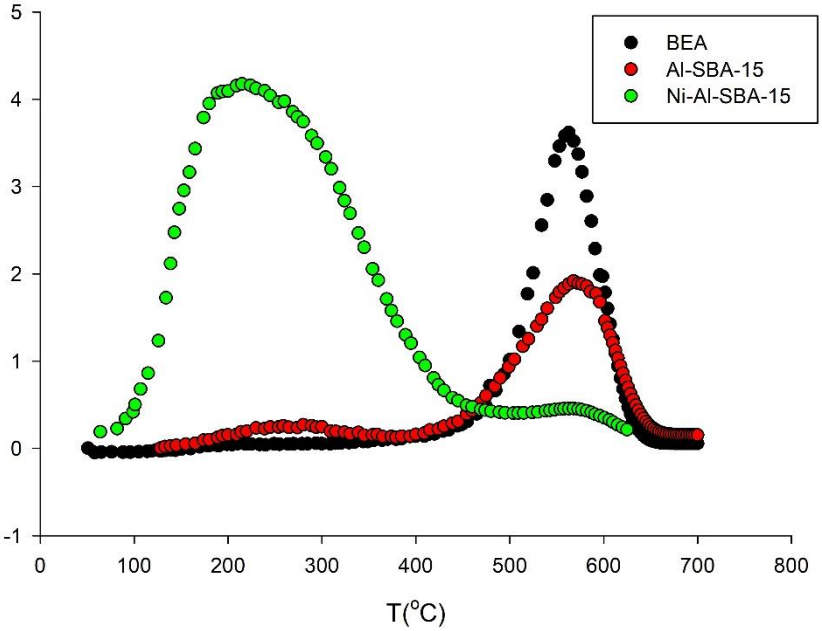


Figure 1: NH_4-TPD profiles for Al-SBA-15 and Ni-Al-SBA-15. Zeolite BEA for reference (m/z = 16).

The TPD measurements (Figure 1) demonstrate that substantial Brønsted acidity, comparable to H-BEA was engendered into the SBA-15 support through the addition of aluminum into the framework. Adding nickel at 20 wt% however, decreased the population of strong acid sites substantially, with weak acid sites dominant. We believe that this may be due to a decrease in the ratio of Brønsted to Lewis acid sites, and to a lesser extent the relaxation of the Si-O(H)-Al bond angle, known to occur readily in amorphous materials[3].

Reaction Data: The nickel-free Al-SBA-15 does not exhibit high activity in either hydrogenation or cracking of the phenanthrene PAH. This is to be expected, as the metallic Ni site is active for hydrogenation and cracking does not occur to a great extent on resonance-stabilized structures, namely aromatic rings. To the extent that the phenanthrene is converted (25%), the primary product is methane. The Nickel-BEA catalyst exhibits significantly higher phenanthrene conversion (86%), with the primary products being phenanthrene hydrogenates of varying degrees, propene and ethylene. The greatest phenanthrene conversion for a single catalyst was exhibited by Ni-Al-SBA-15 (96%), with the primary products being hydrogenated phenanthrene analogues and some cracking products such as 1,2-dicyclohexylethane. An experiment with two catalyst beds (Ni-Al-SBA-15, then Ni-BEA) in equal proportion and overall quantity as the previous experiments yielded the highest phenanthrene conversion, at 98%. The primary products in this experiment were one and two-ring cyclic alkanes with various C 1-4 alkane substituents, and a high proportion of propene in the gas product stream. This demonstrates that polyaromatics may be effectively hydrogenated and cracked by the mesoporous catalyst, followed by further cracking and shape selectivity by the zeolite BEA.

References

1. V. Bridgwater, *Biomass Bioenergy* **2012,** *38*, 68-94.
2. P.H. Yan, et. al, *Appl. Catal. B-Environ*. **2020,** *10*.
3. Palčić, A., Valtchev, V., *Appl. Catal. A- General* **2020**, *606*, 117795.

Acknowledgements

The authors would like to acknowledge the ongoing collaboration and sponsorship with Licella Holdings Pty, Ltd.

Catalytic synthesis of adipic acid using biomass-derived raw materials

Maela MANZOLI[*1], Fabio BUCCIOL[1], Sara MORANDI[2], Giancarlo CRAVOTTO[1],
Svetlana IVANOVA[3] and Silvia TABASSO[1]
[1]*University of Turin, Dept. of Drug Science and Technology and NIS Centre, Via P. Giuria 9, 10125, Turin, Italy.*
[2]*University of Turin, Dept. of Chemistry and NIS Centre, Via P. Giuria 7, 10125, Turin, Italy.*
[3]*University of Seville, Dept. of Inorganic Chemistry, Avda. Americo Vespucio 49, 41092, Seville, Spain.*
** maela.manzoli@unito.it*

Significance and Relevance

Adipic acid market in 2022 reached 5.6 Bln $, with a CAGR of 4.8% it is expected to reach 8.2 Bln $ in 2030[1]. At industrial level, it is traditionally produced by Du Pont process[2] involving fossil-type resources and two main steps, the former leading to KA-oil and the latter forming adipic acid by oxidation in HNO_3. Here, more sustainable processes are described, using renewable raw materials to obtain adipic acid. Among the biomass-derived substrates, MW-assisted conversion of 2,5-furandicarboxylic acid over Rh/Al_2O_3 gave the best results (>99% conversion, 78% selectivity) under milder conditions than those reported[2], and opening the way to the possibility of a one-pot reaction.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion and Circular economy
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Adipic acid covers the main market share to produce synthetic fibers, but also finds applications in the production of pharmaceuticals, cosmetics, lubricants, fertilizers and much more[1]. Adipic acid production encompasses different industrial and biotechnological processes[2,3,4], which must face several issues: on one hand, the use of petrol-derived raw materials, NO_x emissions, the use of acids, high cost of H_2O_2 and, on the other hand, low yields and the need to find new bio-synthetic routes and suitable micro-organisms. Therefore, the possibility to design competitive catalytic processes to obtain adipic acid starting from molecules derived from lignocellulosic biomass is of great interest. In this frame, the use of microwaves (MW) guarantees lower heat dispersion due to the MW transparency of the containers allowing rapid heating and temperature homogeneity. This results in both energy savings and an increase in yield and selectivity compared to conventional heating[5], along with a reduction in reaction time. In this study, levulinic acid, mucic acid and 2,5-furandicarboxylic acid were used in the MW-assisted production of adipic acid over different commercial and lab-made catalysts. The optimization of reaction parameters and the effect of the nature of the metal and of the support are investigated.

Materials and Methods

Commercial and lab-made supported metal catalysts were tested in the MW-assisted production of adipic acid (AA) from levulinic acid (LA), mucic acid (MA) and 2,5-furandicarboxylic acid (FDCA). Synthwave multimode microwave (MW) reactor allowing to carry out the reaction under controlled atmosphere and temperature was used. Products were analyzed by GC-MS and GC-FID. TEM, XRD, TGA and FT-IR spectroscopy have been employed to establish structure-activity relationships.

Results and Discussion

The MW-assisted synthesis of adipic acid from levulinic acid afforded mainly γ-valerolactone (GVL), and neither the use of levulinic esters to avoid cyclization produced better results. The conversion of mucic acid (MA) to AA involves a deoxydehydration reaction; various tests led only to the first reaction intermediate, 2,3-dihydroxyhex-4-endioic acid. However, it was not possible to go on with the subsequent steps, obtaining mainly the formation of decarboxylated by-products and lactones. The MW-assisted synthesis of AA starting from FDCA (**Figure 1a**), involves several steps and initially the reaction was divided into two steps: [3,6] in the first one the aromatic system is reduced, while the second

one involves the opening of the furan ring and the elimination of the hydroxyl group with subsequent hydrogenation of the unsaturation produced. As for the first step, complete conversion and selectivity were achieved under operating conditions (140 °C, Pd/C, 10 bar H_2, methanol, 1 hour) much milder than those reported in the literature [5] (140 °C, Pd/SiO_2, 52 bar H_2, acetic acid, 3 hours). Working with water instead of methanol allowed to produce adipic acid in a one-pot reaction (**Figure 1b**). Temperature, pressure, time, amount and type of catalyst (testing different metals and different supports) were varied to obtain the optimized reaction conditions summarized in **Figure 1b**.

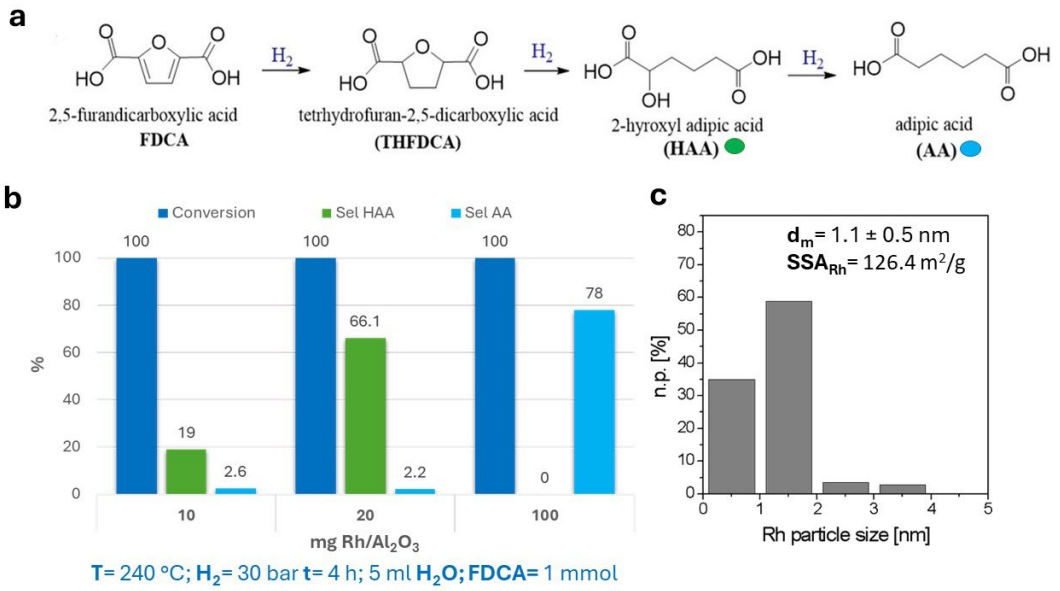


Figure 1. a) Main steps of AA production from FDCA. **b)** Effect of the catalyst amount on conversion and selectivity. **c)** Particle size distribution of the commercial Rh/Al_2O_3 catalyst.

The best catalyst for the optimized reaction was commercial Rh/Al_2O_3: the initial screening of the catalysts revealed first that Rh is more active than Pd and Ru, and furthermore two other catalysts yielded interesting results, namely Rh/TiO_2 and Rh-Re/γ-Al_2O_3 (obtained by US-assisted impregnation with a Rh precursor of ReO_x/Al_2O_3). To correlate the morphological-structural properties to the catalytic activity, an extended characterization was performed on these catalysts. Rh/Al_2O_3 contains homogeneously dispersed nanoparticles with d_m= 1.1± 0.5 nm and a rather narrow size distribution (**Figure 1c**), with 95% of the nanoparticles having size <2 nm (specific surface metal area equal to 126.4 m^2/g of catalyst). Alumina has a rod-like morphology, and it is predominantly amorphous, as confirmed by XRD. Moreover, the results of FT-IR spectroscopy of adsorbed CO indicate that different Rh sites are exposed at the surface of the catalysts depending on the nature of the support. In conclusion, the use of a substrate deriving from renewable resources, combined with microwaves (determining a lower demand for energy consumption) in the presence of a heterogeneous catalyst (easily separable from the substrate) and an aqueous solvent that does not involve toxicity risks allowed to design a more sustainable adipic acid synthesis process.

References

1. https://www.reportsinsights.com/search.php?qry=adipc+acid.
2. Lang, M.; Li, H. *ChemSusChem* **2022**, 15, e202101531.
3. J. C. J. Bart, S. Cavallaro, *Ind. Eng. Chem. Res.* **2015**, 54, 1.
4. E. Skoog, J. H. Shin, V. Saez-Jimenez, V. Mapelli, L. Olsson, *Biotechnology Advances* **2018**, 36, 2248.
5. Roberts, B. A.; Strauss, C. R. Acc. *Chem. Res*. **2005**, 38 (8), 653–661.
6. S. V. de Vyver, Y. Román-Leshkov, Y. *Catalysis Science & Technology* **2013**, 3, 1465.

Acknowledgements

M. M., G.C. and S.T. gratefully acknowledge the University of Turin (Ricerca Locale 2024) for the financial support.

Supercritical Water – Actions and Reactions During the Thermal Decomposition of Plastics

Jack STEEL[1], Taku Michael AIDA[2], Anthony F. MASTERS[1], Alexander K.L. YUEN[1], Thomas MASCHMEYER*,[1]

[1]*The University of Sydney, Laboratory of Advanced Catalysis for Sustainability, School of Chemistry, Sydney NSW 2006, Australia.*

[2] *Fukuoka University, Department of Chemical Engineering, Faculty of Engineering, Nanakuma Jonan-ku, Fukuoka 814-0180, Japan.*

** thomas.maschmeyer@sydney.edu.au*

Significance and Relevance

As the demand for sustainable solutions increases, particularly in the context of climate change, there is a growing need to optimize resource utilization and develop effective pathways for upcycling existing biomass and end-of-life mixed plastic waste to fuels and chemicals. This discussion focuses on the potential of near- and supercritical water for these conversions, which are currently being introduced at scale around the globe.

New work based on model compounds will be used to better describe the multiple modes of action of water and explain why the formation of coke is highly suppressed when using this approach as compared to pyrolysis.

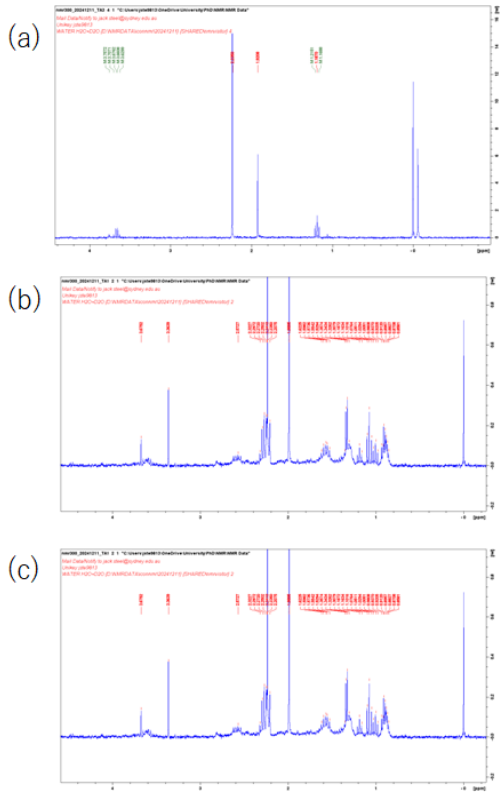
Preferred and 2nd choice for the topic:
(1) Circular Economy; (2) Green Chem. and Biomass Transformation, Renew. Resources Transformation
Preferred presentation: Oral only

Introduction and Motivations

Near- and supercritical water as a solvent dramatically improves the process of pyrolysis for the decomposition of plastics.[1] One of the major advantages is how supercritical water is able to suppress the formation of unwanted chars when compared to pyrolysis.[1] A major factor behind this is the action of water as a solvent or plasticizer; preventing the bimolecular reactions that give rise to larger molecules that form char.[1] But water is not an inert species – it is suspected of acting as a reactant (particularly described as a hydrogen donor) in this process, the pathways of which have yet to be investigated fully.[2] This research will expand upon the roles of water in this process as a reactant, to further our understanding of the pathways present in the HTL environment.

Results and Discussion

Does water react itself as a radical during the hydrothermal decomposition of polymers? There is conflicting evidence present in the literature as to the source of oxygenated compounds formed in this reaction. Oxygenates could be formed from water acting as a reactant or it could be formed from oxygen or air present in the reactor at the time of conducting the reaction. Using 1-dodecene as a model compound, we have investigated this further. When 1-dodecene is reacted under either pyrolysis or supercritical water conditions with an atmosphere of air inside the reactor, the organic phase consists predominantly of hydrocarbon species. However, several oxygenated species (e.g. methanol and other alcohols) can be detected in the aqueous phase post reaction via NMR. When the air atmosphere is replaced with argon, these oxygenates disappear from the product slate. Therefore, we conclude that the oxygen from air is responsible for the oxidation of the starting material to form all oxygenated products. Thus, when air or oxygen is present in the reactor to any extent, a small degree of supercritical water oxidation reactions are occurring in addition to pyrolysis, resulting in the formation of oxygenated species.



Additionally, we have sought to investigate the reactions that are responsible for the formation of aromatic molecules in the decomposition of waste tyres. The formation of aromatics has often been attributed to a Diels-Alder reaction that forms the cyclic structure, followed by a subsequent dehydrogenation reaction. Our results from the decomposition of tyres indicate that there is a different aromatization pathway possible for these substrates.

Limonene, a major product formed during pyrolysis of tyres, appears to aromatise to form p-cymene in the hydrothermal reactor.

The aromatics formed have a specificity for this isomer that is likely as a result of a chain backbiting pathway that forms the cyclic structure. Hydrothermal reactivity of isoprene alone forms a different ratio of isomers. This reaction involves isomerization of the double bond into the ring followed by dehydrogenation and appears to be catalysed by the reactor wall as when performed in a glass ampoule, no reaction is observed for limonene.

Figure 1 H-NMR of the aqueous phase obtained after 1-Dodecene reactions at 450°C and 15 min under reaction conditions; (a) Supercritical water under Ar, (b) Pyrolysis under Air, (c) Supercritical water condition under Air.

In conclusion, our model compound work has elucidated important fundamental reaction paths in SCW that will allow better process design.

References

1. G. Popelier, G. Dossche, S. Kulkarni, F. Vermeire, M. Sabbe, K. van Geem, *J. Anal. App. Pyrol.* **2024**, *183*, 106805.
2. N. Akiya, P. E. Savage, *Chem. Rev.* **2002**, *102(8)*, 2725-2750.

Green Hydrogen from Treated Wastewater via SOECs: A Pathway to Circular Economy and Renewable Energy Integration

Marina MADDALONI[1], Matteo MARCHIONNI[3], Alessandro ABBÁ[1], Michele MASCIA[3], Vittorio TOLA[3], Maria Paola CARPANESE[4], Giorgio BERTANZA[1] and Nancy ARTIOLI[1]*

[1]Department of Civil, Environmental, Architectural Engineering and Mathematics, University of Brescia, via Branze, 43, 25123 Brescia, Italy

[2]Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), University of Brescia, via Branze 38, 25123 Brescia, Italy

[3]Department of Mechanical, Chemical and Materials Engineering, University of Cagliari, via Marengo 2, 09123 Cagliari, Italy

[4]Department of Civil, Chemical and Environmental Engineering, University of Genova (UNIGEDICCA), via Montallegro 1, 16145 Genoa, Italy

*nancy.artioli@unibs.it

Significance and Relevance

This study demonstrates that Solid Oxide Electrolysis Cells (SOECs) can produce green hydrogen from treated municipal wastewater, presenting an innovative solution to reduce reliance on pure water sources and enhance sustainability. By optimizing thermal energy recovery, the system achieved an efficiency of 85%, generating up to 26.2 kg of hydrogen per cubic meter of wastewater. This novel approach could cover up to 20% of Italy's 2030 energy needs, highlighting SOECs as a feasible technology for circular economy applications in hydrogen production.

Preferred and 2nd choice for the topic:
1st choice: H_2 storage and transportation, green H_2 production, hydrogen vectors;
2nd choice: Water treatment.
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

In pursuit of the European Union's goal of carbon neutrality by 2050, green hydrogen (H_2) has gained significant interest as a low-emission fuel capable of supporting renewable energy storage, decarbonizing industrial processes, and reducing fossil fuel dependency[1]. Among available electrolysis technologies, **S**olid **O**xide **E**lectrolysis **C**ells (**SOEC**s) offer unique advantages for sustainable hydrogen production due to their high efficiency, capability to operate at elevated temperatures, and tolerance to lower-purity water sources[2,3]. This study explores the viability of treated municipal wastewater as a feedstock for **SOEC**s, providing a sustainable alternative that preserves freshwater resources. By utilizing impure water sources and recovering energy efficiently, **SOEC**s not only offer a pathway to green hydrogen production but also support circular economy principles through wastewater reuse.

Materials and Methods

Four distinct wastewater streams from Northern Italian municipal **W**aste**W**ater **T**reatment **P**lants (**WWTP**s) were analyzed, each with unique characteristics, such as population capacity, industrial load, and treatment methods. The wastewater samples were pre-treated, and pollutant concentration levels were assessed against Italian regulatory limits for discharge into surface water and public sewers. Using the *Aspen Plus* simulation platform, the **SOEC** process was modeled with a focus on the evaporative potential of each wastewater stream, as well as the thermal integration within the **SOEC** stack to minimize external energy input. The **SOEC** model included energy and mass balance equations for heat exchangers and split junctions, taking into account temperature, mass flow, and electrochemical reactions within the cell. This simulation framework enabled the estimation of hydrogen production efficiency, energy consumption, and potential environmental impact.

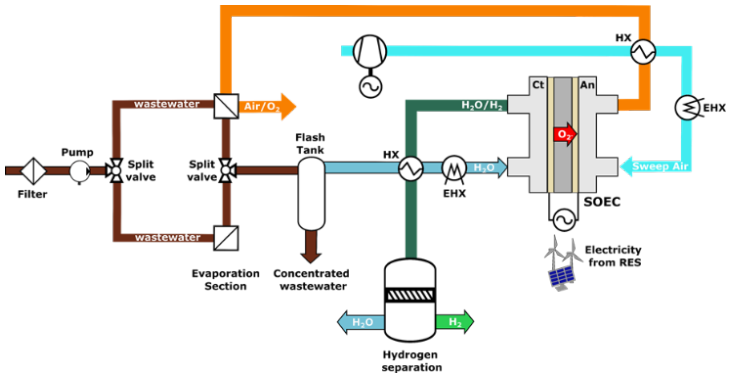


***Figure 1**. Layout of the SOEC stack.*

Results and Discussion

This study demonstrates that treated municipal wastewater from various WWTPs, differing in capacity, industrial load, and treatment methods, can serve as an effective and sustainable water source for SOEC-based green hydrogen production. With the European Union's energy transition goals, Italy aims to install 5 GW of electrolysis capacity by 2030, and wastewater-fed SOECs present a promising strategy to meet this target by reducing dependency on high-purity water sources.

In the Best-case Scenario (BS), where the SOEC operates for 7,500 hours annually with a moderate power setting of 2.12 V and supported by a mix of wind and conventional energy, two WWTPs were evaluated for their potential hydrogen contributions. WWTP C, with a capacity of 120,500 population equivalent (P.E.), an average flow rate of 27,500 m^3/day, and an industrial load of 11%, could produce 0.10 Mt/y of hydrogen, equating to roughly 15% of Italy's national target. Meanwhile, the larger WWTP A, with a capacity of 620,600 P.E., a flow rate of 155,300 m^3/day, and a 15% industrial load, could generate 1.46 Mt/y of hydrogen—well above the national goal. Even under a more constrained scenario (Worst-case Scenario, WS), where SOEC operation relies solely on wind energy and is limited to 2,000 hours annually, WWTP A still shows a significant output with 0.39 Mt/y of hydrogen, while WWTP C contributes 0.03 Mt/y.

Converting these hydrogen outputs into potential electricity contributions highlights the substantial role that wastewater-based SOECs could play in Italy's future energy landscape. Meeting Italy's projected electricity demand growth in 2030 will require the addition of 8.6 to 10.7 GW of new capacity per year. Under BS conditions, WWTP A alone could fulfill 20% of this additional capacity requirement, while it could still meet 5.4% in the WS. Similarly, WWTP C could supply 1.3% in the best scenario and 0.4% in the worst scenario. These findings underscore the significant renewable energy potential of wastewater-fed SOECs, supporting Italy's transition toward a sustainable and decarbonized electricity grid.

References

1. European Commission, Communication from the commission to the European parliament, the council, the European economic and social committee and the committee of the regions - A European strategy for data, 2020.
2. D. F. Di and L. Setti, 2022, 1–40.
3. M. A. Laguna-Bercero, J. Power Sources, 2012, 203, 4–16.

Acknowledgements

The authors thank the European Union for funding this research through the NextGenerationEU program under the PROMETH2eus project.

Ni exsolved nanoparticles from a $La_{1-\alpha}Ni_{1-x}Cr_xO_3$ perovskite for Methane Steam Reforming

María A. ORTEGA-JÁUREGUI[*1, 2], Deblina MAJUMDER[3], Evangelos I. PAPAIOANNOU[3] Francisco GARCÍA-GARCÍA[2], Elodie BLANCO[1], Néstor ESCALONA[1]

[1] *Departamento de Ingeniería Química y Bioprocesos, Escuela de Ingeniería, Pontificia Universidad Católica de Chile, Macul, Santiago, Chile.*
[2] *Institute for Materials and Processes, School of Engineering, University of Edinburgh, Edinburgh, Scotland, United Kingdom.*
[3] *Materials, Concepts & Reaction Engineering (MatCoRE) Group, School of Engineering, Newcastle University, Newcastle upon Tyne, United Kingdom.*
**mnortega@uc.cl*

Significance and Relevance

Exsolution is promising in catalysis due to its ability to produce uniformly distributed, anchored metallic nanoparticles, enhancing resistance to coking and agglomeration. ABO_3 perovskites, such as $La_{1-\alpha}Ni_{1-x}Cr_xO_3$, provide ideal structural stability and flexibility for this process. The reducibility of the B-site cation, like nickel, is vital for nanoparticle formation in applications like methane steam reforming. Additionally, A-site vacancies induce distortions that facilitate cation migration, partial substitution at the B-site is necessary to preserve the integrity of the perovskite structure. The $La_{1-\alpha}Ni_{1-x}Cr_xO_3$ design integrates these attributes, offering a highly efficient and stable catalyst for advanced catalytic applications.

Preferred and 2nd choice for the topic: H_2 storage and transportation, green H_2 production, hydrogen vectors
Preferred presentation: Oral only

Introduction and Motivations

The Methane Steam Reforming (MSR) is the most commonly used process for hydrogen production from fossil fuels due to its high hydrogen-to-carbon ratio and low by-product formation compared to other methods[1,2]. Although this conventional reforming method is well-established, it comes with several drawbacks. One major issue is the deactivation of catalysts due to sintering or coke formation at high temperatures, which leads to a decline in catalytic activity[3, 4].

This study focuses on utilizing exsolution from an ABO_3 perovskite as a method for synthesizing well-dispersed metallic nanoparticles that are anchored to their matrix. This approach enhances stability and resistance to carbon deposition. Specifically, the ongoing research evaluates the catalytic activity and stability in MSR using exsolved Ni nanoparticles from a $La_{1-\alpha}Ni_{1-x}Cr_xO_3$ perovskite. The investigation includes examining stoichiometric factors, A-site deficiencies, and partial substitution of the B-site.

Results and Discussion

The $La_{1-\alpha}Ni_{1-x}Cr_xO_3$ perovskites were prepared using the Pechini sol-gel method, as illustrated in Fig. 1A. The reactions conducted thus far (see Fig. 1B) have demonstrated enhanced performance during the second run for stoichiometric perovskites ($\alpha = 0$), suggesting **exsolution and reconstruction processes driven by the feed gas**. Notably, the sample with no partial substitution (S1) achieved 100% conversion of CH_4 at approximately 600°C in the second run, showing higher conversion rates at lower temperatures compared to traditional catalysts. **Furthermore, the exsolved nanoparticles from A-site deficient perovskites displayed initial catalytic activity at lower temperatures than their stoichiometric counterparts**.

These findings, supported by characterization reports, imply successful production of exsolved Ni nanoparticles from A-site deficient perovskites. **They also demonstrate higher crystallinity or an increased surface quantity of Ni^0 under exsolution conditions (H_2 atmosphere)**. Significantly, these conditions create active sites that facilitate reactions at lower temperatures than conventional industrial catalysts, highlighting their potential for further stability assessments.

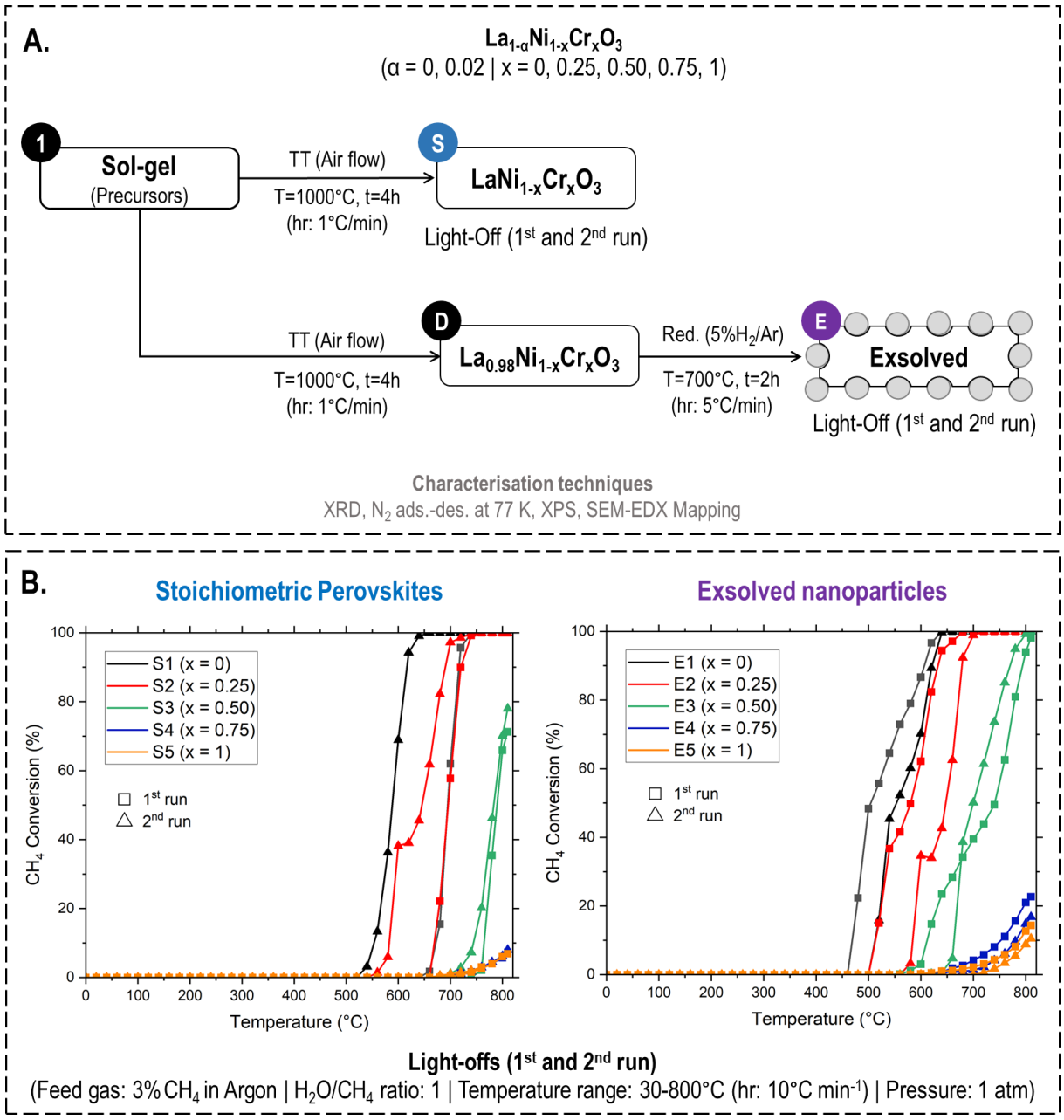


Fig. 1. Schematic summary showing A. the synthesis route and experimental conditions for the preparation of stoichiometric (S) and A-site deficiency (D) perovskites and exsolved nanoparticles (E), and B. light-offs for methane steam reforming reaction.

References

1. Castro-Dominguez, B., Mardilovich, I. P., Ma, L. C., Ma, R., Dixon, A. G., Kazantzis, N. K., & Ma, Y. H. *Membranes* **2016**, 6(3).
2. LeValley, T. L., Richard, A. R., & Fan, M. *Energy* **2015**, 90, 748–758.
3. Nieva, M. A., Villaverde, M. M., Monzón, A., Garetto, T. F., & Marchi, A. J. *Chemical Engineering Journal* **2014**, 235, 158–166.
4. Halabi, M. H., De Croon, M. H. J. M., Van Der Schaaf, J., Cobden, P. D., & Schouten, J. C. *Applied Catalysis A: General* **2010**, 389(1–2), 68–79.

Acknowledgements

ANID (Chilean National Research and Development Agency) for the PhD programme fundings.
Proyecto Anillo ACT240050.

Tailoring catalytic activity of MoS_2 catalyst through functionalization with Brønsted-acid ligands: A Computational and experimental study for enhanced Hydrogen Evolution Reaction in Alkaline Media

Ida Ritacco*[,1], Giuseppe Santoriello[1], Giulia Tuci[2], Giuliano Giambastiani[2], Matteo farnesi Camellone[3], Lucia Caporaso[1]

[1]*Dipartimento di Chimica e Biologia, Università degli Studi di Salerno, via Giovanni Paolo II 132, 84084 Fisciano, Salerno, Italy*

[2]*Institute of Chemistry of OrganoMetallic Compounds, ICCOM-CNR and Consorzio INSTM, Via Madonna del Piano, 10 - 50019, Sesto F.no, Florence, Italy.*

[3] *Consiglio Nazionale delle Ricerche-Istituto Officina dei Materiali (CNR-IOM), 34136 Trieste, Italy*

** iritacco@unisa.it*

Significance and Relevance

The hydrogen evolution reaction (HER) conducted in alkaline electrolytes represents a crucial breakthrough for the sustainable development of hydrogen production as a green fuel. In this context, the surface functionalization of chemically exfoliated MoS_2 flakes with strongly Brønsted-acid end-capped aryl fragments, such as sulfonic (Ar-SO_3H) acids,[1,2] has been found to be surprisingly effective for HER in alkaline environments, where water dissociation typically acts as the bottleneck. DFT calculations, combined with ab initio molecular dynamics simulations (AIMD), reveal the mechanisms behind this unexpected but desirable behavior, demonstrating how this engineering-based functionalization creates an ideal surface microenvironment that efficiently promotes HER, with kinetics surprisingly independent of the acidic or basic nature of the electrolyte.

Preferred and 2nd choice for the topic: Oral
Preferred presentation: **Short Oral**

Introduction and Motivations

The HER conducted in alkaline electrolytes could pave the way to produce hydrogen as a green fuel, as it enables the use of cost-effective and abundant transition metal-based catalysts.[3] However, the slow water dissociation kinetics in alkaline environments still hinders its development.[4,5]

Recent advances have highlighted the potential of transition metal dichalcogenides, such as MoS_2, as low-cost, effective alternatives for HER catalysis.[6] However, molybdenum disulfide still faces challenges, including hydrophobicity and limited performance in alkaline conditions. Surprisingly, chemically exfoliated MoS_2 flakes functionalized with Brønsted-acid end-capped aryl groups, such as carboxylic (Ar-COO^-) and sulfonic (Ar-SO_3^-), have shown activity in HER under pH conditions dependent on the acid strength of the pendant group.[7] With the goal of designing and developing more efficient catalysts for HER in alkaline environments, this unexpected behavior was rationalized through a detailed theoretical study. The electronic and steric properties of these modified surfaces, together with mechanistic insights into the water dissociation process and molecular dynamics simulations, helped define the kinetic framework and clarify the relationship between catalytic performance in alkaline environment and the chemical and electronic nature of the surface modification.

Results and Discussion

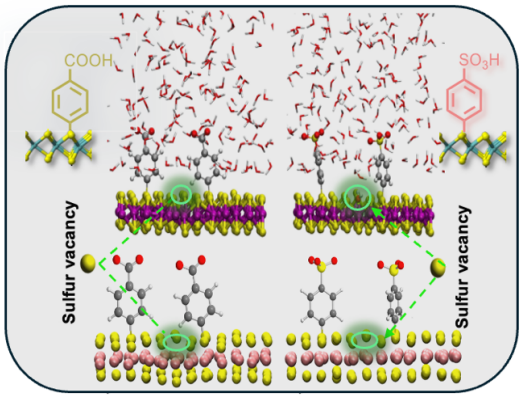
This study explores how sulfur vacancies (Vs) and surface functionalization with Brønsted-acid end-capped aryl fragment ligands impact the hydrogen evolution reaction (HER) activity of 1T-MoS_2-based catalysts. Specifically, we focus on the Volmer step in the HER process, which involves water adsorption on the catalyst surface and its subsequent dissociation to form H* and OH* species, a key rate-determining step in alkaline media.[8] We computed the adsorption energies of H_2O on both stoichiometric and sulfur-defective 1T-MoS_2 catalysts, including functionalized models (1T-MoS_2@2COO^- and 1T-MoS_2@2SO_3^-). Our results show that water adsorption is thermodynamically unfavorable on stoichiometric 1T-MoS_2 due to repulsive interactions with sulfur atoms. In contrast, sulfur-defective catalysts exhibit significantly stronger water adsorption, especially when

functionalized with ligands that further stabilize the system by enhancing the exposure of molybdenum (Mo) sites, as observed with Ar-SO_3^-.

Through nudged elastic band (NEB) calculations, we found that the presence and nature of the organic ligands significantly influence the overall reaction kinetics. The aromatic ligands, interacting with hydrogen atoms from the water molecules, guide the water toward the channel formed by neighboring ligands, facilitating its approach to the surface. Notably, the vacancy site interacts more readily with water only in the case of the Ar-SO_3^- ligand, which facilitates the subsequent dissociation step, in agreement with experimental data.

Additionally, ab initio molecular dynamics (AIMD) simulations confirmed that the wettability of the catalysts improves in the presence of sulfur vacancies. Specifically, 1T-MoS_2@Vs@2SO_3^- exhibited enhanced hydrophilicity, while 1T-MoS_2@Vs@2COO^- remained hydrophobic due to interactions between the vacancy and the ligand.

In conclusion, this study demonstrates that sulfur vacancies and surface functionalization with organic ligands significantly influence both water adsorption and dissociation, offering valuable insights for optimizing HER catalysts under alkaline conditions. Our findings suggest that tuning vacancy sites and ligand chemistry can enhance the catalytic efficiency of 1T-MoS_2-based materials, enabling efficient hydrogen production across a broad pH range and advancing the design of HER catalysts.



References

1. Amores, E.; Sánchez, M.; Rojas, N.; Sánchez-Molina, M., *Eds. Academic Press*, **2021**,271-313.
2. Terlouw, T.; Bauer, C.; McKenna, R.; Mazzotti, M., *Energy Environ. Sci.* **2022**, *15*, 3583-3602.
3. Salvò, D.; Mosconi, D.; Neyman, A.; Bar-Sadan, M.; Calvillo, L.; Granozzi, G.; Cattelan, M.; Agnoli, S., *Nanomaterials* **2023**, *13(4)*, 683;
4. Xu, Y.; Ge, R.; Yang, J.; Li, J.; Li, S.; Li, Y.; Zhang, J.; Feng, J.; Liu, B.; Li, W., *J. Energy Chem.* **2022**, *74*, 45-71.
5. Li, Y.; Zhang, Y.; Tong, X.; Wang, X.; Zhang, L.; Xia, X.; Tu, J., *J. Mater. Chem. A* **2021**, *9*, 1418-1428.
6. Xu, J.; Shao, G.; Tang, X. et al, *Nat Commun* 2022, *13*, 2193.
7. Giambastiani, G. et al. submitted.
8. Dong, F.; Zhang, m.; Xu, X.; Pan, J.; Zhu, L.; Hu, J., *Nanomaterials* **2022**, *12*, 4273.

Acknowledgements

Lucia Caporaso acknowledges:

Funder: Project funded under the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3 - Call for tender No. 1561 of 11.10.2022 of Ministero dell'Università e della Ricerca (MUR); funded by the European Union – NextGenerationEU.

Award Number: Project code PE0000021, Concession Decree No. 1561 of 11.10.2022 adopted by Ministero dell'Università e della Ricerca (MUR), CUP - B53C22004060006, Project title "Network 4 Energy Sustainable Transition – NEST"

Platinum-Tin Encapsulated Zeolite Catalysts with High Sn Loading: Boosted Performance in Methylcyclohexane Dehydrogenation

Wei SHI[1], Akira ODA*[,1], Yuta YAMAMOTO[2], Kyoichi SAWABE[1], Atsushi SATSUMA[1]
[1]*Department of Materials Chemistry, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan.*
[2] *Institute of Materials and Systems for Sustainability, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan.*
**e-mail : akira@chembio.nagoya-u.ac.jp*

Significance and Relevance

In this study, Pt-Sn bimetallic catalysts were designed for the first time with a high Sn content (2.8 wt.%-3.9 wt.%, Sn/Pt ratio = 6-8) in zeolite mother gel for methylcyclohexane (MCH) dehydrogenation. A well-defined Pt_1Sn_6@S-1 catalyst with a unique Pt core-Sn shell structure was prepared via a facile one-pot hydrothermal synthesis method. This encapsulated catalyst exhibited excellent catalytic performance and overwhelming superiority over supported catalysts, showing high activity (1343 $\mathrm{mmol}_{!\ ¡}/\mathrm{g}_{"\#}/\mathrm{min}$), toluene (TOL) selectivity (~100%), and durability (>80% for 33 h).

Introduction and Motivations

MCH dehydrogenation to TOL is one of the desired reaction systems for hydrogen storage and production due to its low toxicity, high reusability, and high hydrogen density.[1]. Pt-based catalysts are currently the mainstream materials for this reaction, but these catalysts still suffer from insufficient activity, low selectivity, and short-term stability. The further improvement of catalytic performance is of great significance for the application of MCH catalysts. Alloying with Sn could effectively modify the local structure of Pt,[2] thus promoting the performance; encapsulating Pt-Sn species in zeolite matrix could prevent sintering,[3] achieving high activity and stability. Herein, PtSn@S-1 catalysts were prepared, and the structure-property relationship was systematically studied.

Materials and Methods

The catalysts were prepared by a one-pot hydrothermal synthesis method.[4] The Pt and Sn precursor solution with different Sn/Pt ratios, tetrapropylammonium hydroxide, tetraethyl orthosilicate and deionized water were mixed and stirred for 6 h to prepare the zeolite mother gel. After hydrothermal treatment (170 °C for 3 d), followed by centrifugation, drying (80 °C for overnight) and H_2 reduction (400 °C for 2 h), the encapsulated Pt_1Sn_x@S-1 (x = 1, 4, 6, 8) catalysts were obtained. The activity test was performed at 300 °C using 50 mg of catalysts, and the feeding gas was 1.6% MCH/Ar (20 ml/min). The durability test was measured at 350 °C and co-fed with 1.6% MCH, 5% H_2 and Ar balance.

Results and Discussion

The Pt_1Sn_6@S-1 catalyst with high Sn loading (2.8 wt.%) was successfully prepared for MCH dehydrogenation with a H_2 revolution rate of 1343 $\mathrm{mmol}_{!\ ¡}/\mathrm{g}_{"\#}/\mathrm{min}$ (Fig. 1a), which was nearly twice the activity of the reported best catalyst.[5] The well formation of zeolite particles in MFI-type for these PtSn@S-1 catalysts with high Sn loading was confirmed by HAADF-STEM and XRD. Despite the high Sn/Pt ratio, the Pt nanoparticles in Pt_1Sn_6@S-1 was well dispersed with average size of only 1.4 ± 0.5 nm (Fig. 1b). On the contrary, Pt_1Sn_6/S-1 presented terrible Pt dispersion with a much higher Pt nanoparticle size of 3.1 ± 1.8 nm (Fig. 1c). Compared with supported Pt_1Sn_6/S-1, no XPS signals of Pt could be observed for Pt_1Sn_6@S-1 catalysts (Fig. 1d), confirming the encapsulation of Pt in S-1 zeolite matrix. Although Sn primarily exists in an oxidized form in both Pt_1Sn_6@S-1 and Pt_1Sn_6/S-1 (Fig. 1d), Sn in Pt_1Sn_6@S-1 were mainly framework Sn species, whereas Sn in Pt_1Sn_6/S-1 were extra-framework Sn species on the surface of zeolite proved by UV-Vis. Combined with the characterization of CO-FTIR and WT-EXAFS, a unique Pt core-Sn shell structure was confirmed for Pt_1Sn_6@S-1 catalyst.

As shown in Fig. 1e, the initial activity (at 10 min) could be significantly improved along with the Sn/Pt ratio, and Pt_1Sn_6@S-1 showed the highest MCH conversion rate without H_2. The PtSn@S-1 catalysts with high Sn/Pt ratio of 6-8 presented minimal differences between initial activity and final activity (at 60 min), showing good stability. The selectivity of Pt_1Sn_6@S-1 have been checked by IR

spectra, and no peak assigned to by-product CH_4 could be detected, confirming the high TOL selectivity. The long-term stability of PtSn@S-1 catalysts were further measured and excellent durability (>80% for 33 h) was demonstrated for Pt_1Sn_6@S-1 even under a harsher condition (WHSV= 120,000 ml/g/h). Though a slight deactivation could be observed for Pt_1Sn_6@S-1 catalyst, this catalyst could be effectively regenerated by H_2, further confirming its excellent performance. The origin of this excellent performance has been further studied by MCH breakthrough curve, TOL-TPD, and the state of active sites after reaction.

In summary, Pt-Sn nanoparticles were successfully encapsulated within the S-1 zeolite matrix even with such high Sn loadings (2.8 wt.%-3.9 wt.%). These PtSn@S-1 catalysts demonstrated excellent activity, selectivity and durability for MCH dehydrogenation. A unique Pt core-Sn shell structure was generated over Pt_1Sn_6@S-1 catalyst. Owing to it, the electronic environment of Pt was altered and the TOL desorption properties were enhanced, thereby leading to excellent performance.

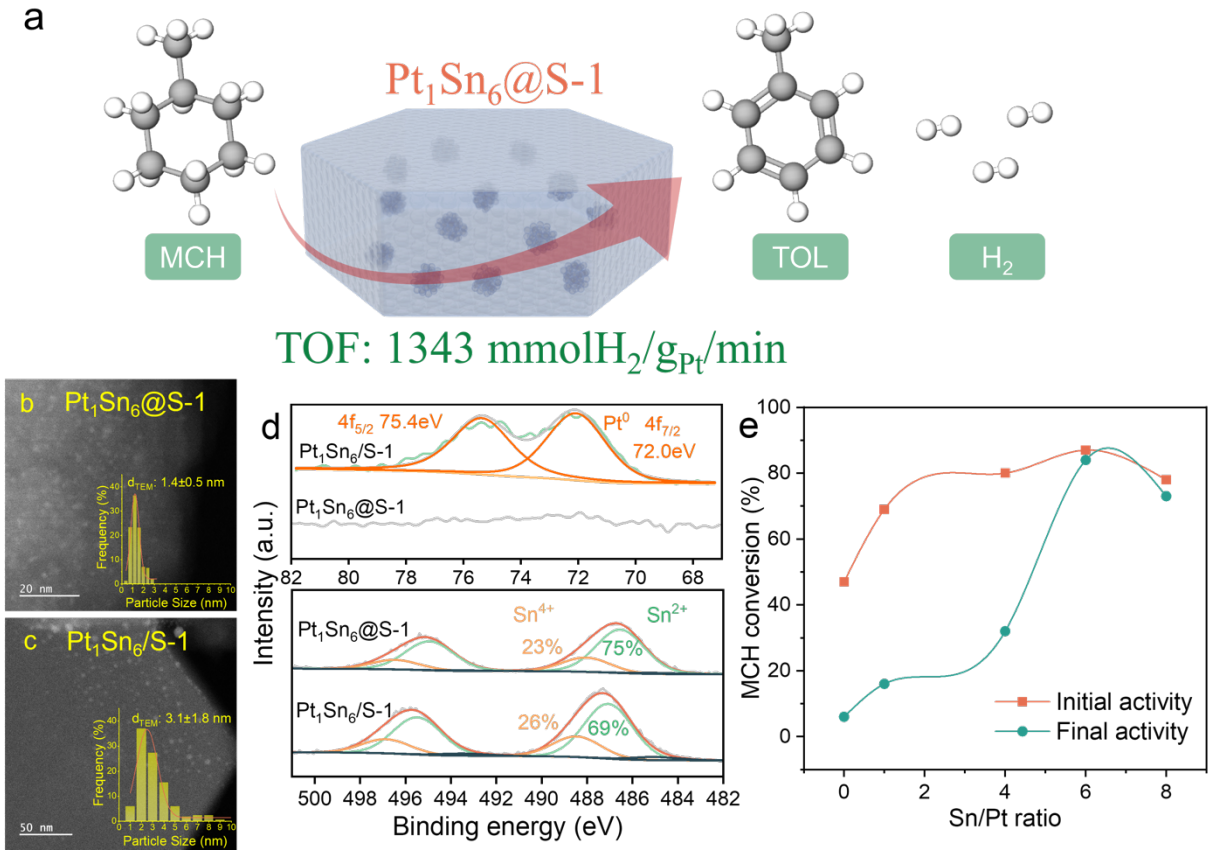


Figure 1 (a) Scheme of MCH dehydrogenation over Pt_1Sn_6@S-1; (b-c) HAADF-STEM images and (d) Pt 4f and Sn 3d XPS spectra of Pt_1Sn_6@S-1 and Pt_1Sn_6/S-1; and (e) activity test of PtSn@S-1 catalysts.

References

1. E. Gianotti et al., *ACS Catal.*, **2018**, *8*, 4660.
2. X. Chen et al., *Nat. Commun.* **2021**, *12*, 2664.
3. L. Liu et al., *Nat. Mater*. **2019**, *18*, 866.
4. Q. Sun et al., *Angew. Chem.*, **2020**, *59*, 19450.
5. Y. Nakaya et al., *ACS Catal*. **2020**, *10*, 5163.

Acknowledgements

This work was supported by Japan Society for the Promotion of Science (JSPS) Grant-in-Aid for Challenging Exploratory Research (24K21807), JSPS Grant-in-Aid for Scientific Research (B) (No. 23K26452), JSPS Grant-in-Aid for Transformative Research Areas (B) (No. 22H05045) and ENEOS Hydrogen Trust Fund. We thanked the staffs of BL5S1 and BL11S2 beamlines of Aichi Synchrotron Radiation Center (AichiSR, Japan) for performing XAFS measurements.

Development of a new perovskite electrocatalyst for solid oxide cells with a novel symmetrical geometry

Amir Yazdani*[1], Gabriella Garbarino[1], Paola Riani[2], Juan Basbus[1], Maria Paola Carpanese[1]
[1] *University of Genoa, Department of Civil, Chemical and Environmental Engineering (DICCA), Via Opera Pia 15, 16145 Genoa, Italy.*
[2] *University of Genoa, Department of Civil, Chemical and Environmental Engineering (DCCI), Via Dodecaneso 31, 16146 Genoa, Italy.*
**** amir.yazdani@edu.unige.it***

Significance and Relevance

In this work, new electrocatalytic material has been developed for reversible solid oxide cells in order to not only increase their performance and chemical stability, particularly against seawater vapour environment and oxygen atmosphere, but also use safe raw materials for both humans and the environment (Co and Ni free electrode). The important obtained result is that this kind of reversible solid oxide is capable of having very low resistance during H_2 production. Moreover, to optimize the structure of the global cell having a symmetrical geometry, an isotropic morphology has been designed capable of increasing the gas diffusion within the electrodes and ensuring mechanical stability in case of high partial pressures in the electrolysis mode of operation.

Introduction and Motivations

According to the objectives of numerous countries globally, the urgent need to decarbonize economies and provide energy security is what is driving the global energy transition. A prominent factor of this endeavour is the hydrogen economy, which serves as a versatile and sustainable energy source for use in transportation, manufacturing, and other fields. Water electrolysis is one of the most environmentally friendly ways to produce hydrogen, especially when it is coupled with renewable energy[1]. Traditional electrolysis depends on freshwater, which is poor in many areas. On the other hand, the vast quantities of seawater (or other non-potable water sources) would provide a nearly unlimited water supply if saline water could be used directly as a clean energy source. In this frame of usage of direct seawater, the design and optimization of the electrodes, which are usually different for fuel oxidation and oxygen reduction processes, is a crucial problem in SOC technology. In order to simplify the cell manufacture, lower the costs, and improve the cell durability, the idea of symmetrical electrodes—where the same material is used for both the anode and the cathode—has attracted plenty of attention recently[2]. By removing the need for several materials with distinct thermal and chemical compatibility criteria, symmetrical electrodes solve problems like interfacial deterioration and thermal expansion mismatches. In addition to optimizing production procedures, this strategy opens the door for reliable and effective SOC technologies that may fulfil the needs of the emerging energy scenario.

Materials and Methods

The perovskite-based electrode materials $Ba_{0.5}Sr_{0.5}Fe_{0.9}Mo_{0.1}O_{3-\delta}$ were synthesized through the sol-gel method. The resulting powders were characterized by Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD), which are reported in Fig. 1. Electrochemical impedance spectroscopy (EIS) measurements were conducted in electrolyte-supported and complete button cells to test their performance in electrolysis and fuel cell operating mode[3]. The current-voltage characteristics were extracted to show competitive performance with the state-of-the-art materials in both operating modes (electrolytic and fuel cell mode) and in both environments (H_2/H_2O and O_2)[4].

Results and Discussion

The data analysis showed $Ba_{0.5}Sr_{0.5}Fe_{0.9}Mo_{0.1}O_{3-\delta}$can provide high electrochemical performance in terms of polarization resistance if compared to other Co-free materials. The distribution of relaxation times analysis performed on the impedance results subsequently demonstrated the impact of O_2 and H_2/H_2O partial pressure and temperature. Moreover, under a cyclic process, it was found that the mentioned electrode takes back its structure in an oxidizing environment after it is subjected to a reducing atmosphere. In the oxygen environment, the performance of the electrode appeared

promising while its performance in the reducing environment is currently being carried out. In the end, materials were deposited on two different solid oxide electrolytes (Gd-doped ceria and $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.8}O_{3-\delta}$) and found compatible with them at the operating temperature.

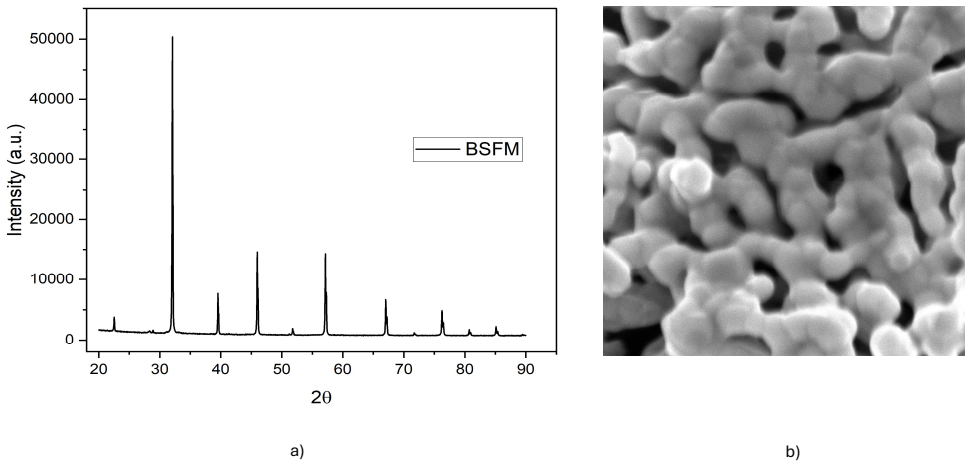


Figure 1: a) the structural characterisation b) the morphological characterization, of the BSFM electrocatalyst

References

1. Zhang, Panpan, et al. ACS Sustainable Chemistry & Engineering 12.4 (2024): 1561-1572.
2. Fang, Liyang, et al. ACS Applied Materials & Interfaces 16.16 (2024): 20419-20429.
3. Marasi, Martina, et al. Journal of Power Sources 555 (2023): 232399.
4. Rehman, Saeed Ur, et al. Applied Catalysis B: Environment and Energy 333 (2023): 122784.

Acknowledgements

The authors thank the support of the Italian project PROMETH2eus (ID: RSH2A_000039-CUP: F37G22000080006) funded by the Next Generation EU (Piano Nazionale di Ripresa e Resilienza-PNRR, Missione 2, Componente 2) and coordinated by DICCA - University of Genoa.

Assessment of solar-to-chemical efficiency using only electrolyzer characteristics Shortcut bridging electrochemistry and photovoltaics

Oleksandr ASTAKHOV*,1, Thérèse CIBAKA[1], Lars WIEPRECHT[1], Uwe RAU[1,2], Tsvetelina MERDZHANOVA[1]
[1] *Photovoltaics (IMD-3), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany.*
[2] *Faculty of Electrical Engineering and Informa Technology, RWTH Aachen University, Mies-van-der-Rohe-Straße 15, 52074 Aachen, Germany.*
** o.astakhov@gmail.com*

Significance and Relevance

We developed a new rapid method to assess the Solar-to-Chemical efficiency (STC) potential of electrochemical (EC) cells and stacks with any photovoltaic (PV) device under any irradiance at any relative PV-to-EC scaling and any mode of power coupling. The method does not require numerical simulations or modelling of the PV-EC systems. This comprehensive overview is achieved via a mathematically simple conversion of the EC characteristics in any spreadsheet software. The method is demonstrated via the analysis of CO2-reduction electrolyzer characteristics and verified with dedicated PV-EC experiments.

Preferred and 2nd choice for the topic: Photocatalysis and photoelectrocataly approaches, solar energy u iza n; Sustainable and clean energy produ on and transport
Preferred presen on: (Oral only)

Introduction and Motivations

Electrochemical (EC) devices represent a promising solution for solar energy storage and industry decarbonization once combined with Photovoltaics (PV) in PV-EC systems. The development of PV-EC systems requires interdisciplinary collaborative efforts of different research groups from both photovoltaic and electrochemical research communities. Therefore, testing a new electrolyzer with a chosen PV device to evaluate its Solar-to-Chemical (STC) efficiency potential can be a difficult and time-consuming task. To minimize the effort, we developed a new rapid method for assessing the STC that an electrolyzer can achieve in combination with PV of any efficiency and scale under any irradiance and mode of coupling. Using basic power balance rules typical EC characteristics are unfolded into the parameter space of PV-EC systems and subsequently to STC. The pairwise correspondence of system parameters and STC allows to establish a map of STC attainable by the electrolyzer in any PV-EC scenario without system modelling. This comprehensive overview is achieved via a mathematically simple conversion of the EC characteristics and can be performed with any spreadsheet software. The method is based on our previous work on the "reverse analysis" of the solar-to-hydrogen efficiency limit in PV-EC water splitting systems[1]. In this work, we generalize the method for treating electrolyzers with an arbitrary number of products, nonideal Faradaic efficiencies, and various PV-EC system parameters, including coupling efficiency. The method is demonstrated using the characteristics of an experimental CO_2 reduction reaction EC cell with Ag catalyst, which produces CO as the main product and H2 as a byproduct. The results of the analysis are verified by testing the analyzed electrolyzer in combination with high-efficiency concentrator GaAs solar cells.

Materials and Methods

Experimental validation was performed using a CO_2RR microflow electrochemical cell with IrO_2 anode, Ag GDE cathode, and a Nafion 117 cation exchange membrane. Pure CO_2 was directly purged in the cathode compartment. Both the catholyte and anolyte were CO_2 saturated 1 mol L^{-1} $KHCO_3$. The PV-EC experiments were performed with the EC cell direct-coupled to a custom in-house developed PV emulator, which reproduces the required PV current voltage characteristics with precision and accuracy on par with AAA solar simulator [2]. The emulation approach was selected to achieve the necessary flexibility and accuracy in PV scaling, thus ensuring proper coupling to the small-scale laboratory EC device at different area ratios.

Results and Discussion

The proposed analysis procedure addresses (but not limited to) three key PV-EC system parameters: PV efficiency η_{PV} , solar irradiance G , and PV-to-EC area ratio A_R as the minimal set of parameters describing operating conditions of the EC cell. Full set or the analysis results is a part of four dimensional space with three parameter coordinates η_{PV}, G, A_R and the corresponding *STC* values, the dependence of $STC(\eta_{PV}, G, A_R)$. For practical purposes it is convenient to reduce the dimensionality and consider cross sections of the results set as the dependencies of *STC* on one or two parameters while other ones are fixed. Examples of such three dimensional cross sections for $STC(\eta_{PV}, G)$ at constant A_R, $STC(\eta_{PV}, A_R)$ at constant G, and $STC(G, A_R)$ at constant η_{PV} are presented in Figure 1 for the CO product. The results of the validation PV-EC experiments are presented as stars, with the corresponding experimental *STC* values. The mathematically simple unfolding of the EC characteristics leads to a surprisingly comprehensive overview of the EC potential in combination with PV of any size and efficiency under any irradiance. In Figure 1 the *STC* values attainable by the analyzed EC cell in vast variety of PV-coupled scenarios are mapped. The dependencies in Figure 1 are specific to a particular electrolyzer characteristics and any variations of those will change the resulting *STC* maps. This property can be employed to evaluate how variations in EC parameters are projected onto its *STC* potential. By comparing the results obtained at different EC states, operating temperatures, electrolyte compositions, catalyst type, loading, degradation or conditioning, electrolyzer design parameters, etc., variations of these parameters can be systematically evaluated in terms of *STC* limit. Dependencies for the *STC* limit are useful for loss analysis in already tested PV-EC systems, as well as for systems design and comparison. The method provides an easy-to-use shortcut between electrochemistry and photovoltaics, facilitating and streamlining the development of solar chemistry and fuel solutions.

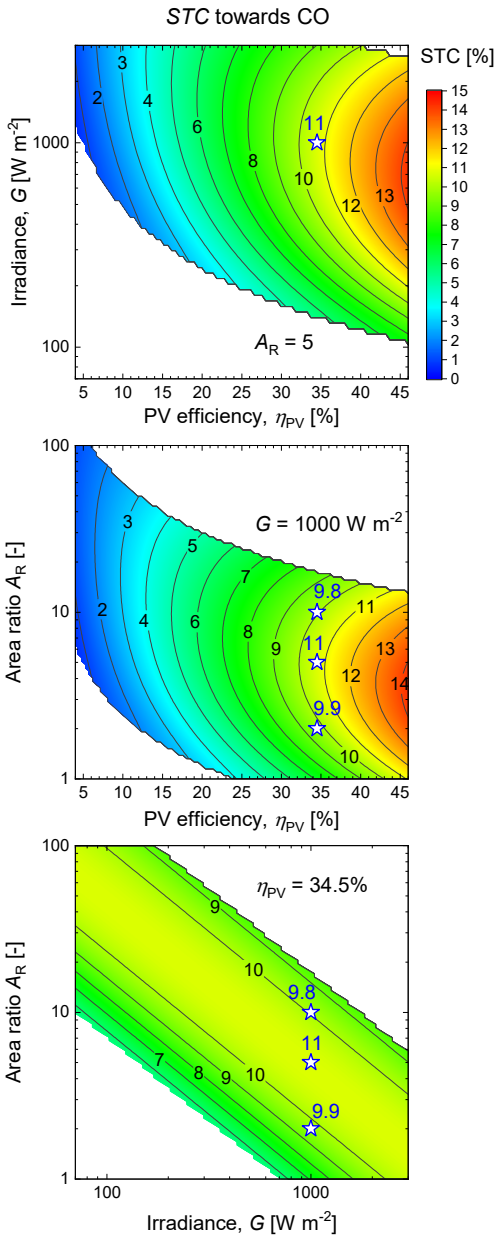


Figure 1 Contour plots of three-dimensional dependencies of (a) STC on η_{PV} and G at constant A_R, (b) STC on η_{PV} and A_R at constant G, and (c) STC on G and A_R at constant η_{PV}. Results of the PV-EC experiment are indicated by stars with STC values next to symbols.

References

[1] O. Astakhov, V. Smirnov, U. Rau and T. Merdzhanova, *Sol. RRL* **2022**, 6, 2100783.
[2] B. P. M. F. Seidler, W. Zwaygardt, S. Haas, O. Astakhov, T. Merdzhanova, *J. Power Sources*, **2024**, under review.

Crystalline face engineering in diverse Bismuth Oxyhalides for enhanced amoxicillin removal from water

Giuseppina CERRATO*[1,2], Alessia GIORDANA[1,2], Vincenzo FABBRIZIO[2,3], Melissa Greta GALLONI[2,3], Ermelinda FALLETTA[2,3], Claudia Letizia BIANCHI [2,3]

[1]*Dipartimento di Chimica, Università degli Studi di Torino, Via Pietro Giuria 7, 10125 Torino, Italy*

[2]*Dipartimento di Chimica, Università degli Studi di Milano, via C. Golgi 19, 20133, Milano, Italy*

[3]*Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), via Giusti 9, 50121 Florence, Italy*

* giuseppina.cerrato@unito.it

Significance and Relevance

Water resources are in growing danger, because of persistent contamination, negative effects driven by climate changes and increasingly demand of water for livestock and agriculture: wastewater purification and reuse is then unavoidable. Advanced oxidation processes (AOPs), such as heterogeneous photocatalysis, have emerged as a promising solution, and the contemporary use of light irradiation and proper semiconductors (above all, TiO_2-based systems) has attracted a lot of interest: recently, research has been focused on different photocatalysts belonging to bismuth oxyhalides (BiOX, in which X represents Cl, Br o I), because of their intrinsic ability in promoting charge carrier separation and thereby enhancing photocatalytic activity.

Preferred and 2nd choice for the topic:
1st choice - Photocatalysis and photoelectrocatalytic approaches, solar energy utilization;
2nd choice - Water treatment
Preferred presentation: Oral only

Introduction and Motivations

In recent decades, the increasing presence of antibiotics in wastewater has become a critical issue: to address this concern, heterogeneous photocatalysis, have emerged as promising solutions[1]. In this context, bismuth-based materials, particularly bismuth oxyhalides (BiOX, where X = Cl, Br, or I), have gained attention due to their easy synthesis, high chemical stability, unique layered structure, and prolonged lifetime of electric charges after light irradiation[2]. The photocatalytic performance of BiOXs can be further optimized by tailoring their (micro)morphology, which significantly influence their surface reactivity and charge dynamics: as an example, in the present research the photocatalytic results obtained for Amoxicillin (AMX) degradation will be presented and discussed.

Results and Discussion

BiOXs are semiconducting materials with a distinctive tetragonal crystal structure in which $[Bi_2O_2]$ slabs are alternated with double slabs of halogen atoms, creating an internal static electric field perpendicular to the layers[3]. This unique configuration facilitates the transport of photo-induced electrons and holes within the crystal, promoting charge carrier separation and thereby enhancing photocatalytic activity. The photocatalytic performance of BiOXs can be further optimized by tailoring their exposed crystal facets: in fact, the growth of specific crystal facets can be tuned by carefully designing the synthesis process, manipulating factors such as (i) reaction temperature and time, (ii) solvent selection, (iii) use of capping agents, and (iv) choice of an appropriate halogen precursor. In this study, the preparation of BiOX photocatalysts, specifically BiOBr and BiOCl, obtained using potassium (K) and calcium (Ca) salts as halogen precursors was thoroughly investigated.

Many different experimental techniques were employed for the characterization of the various BiOX materials under investigation, coupled by a specific photocatalytic experiment devoted to the abatement by photodegradation of amoxicillin (AMX) under simulated sunlight.

Structural and morphological preliminary results indicated there is a peculiar impact of the halogen source on the BiOX crystal structure (as evidenced in Figure 1a), favoring the formation of the (110)

crystal facet when K-salts were used, even though the general ordered "flower-like" morphology, typical of BiOX systems is totally retained (see Figure b and c).

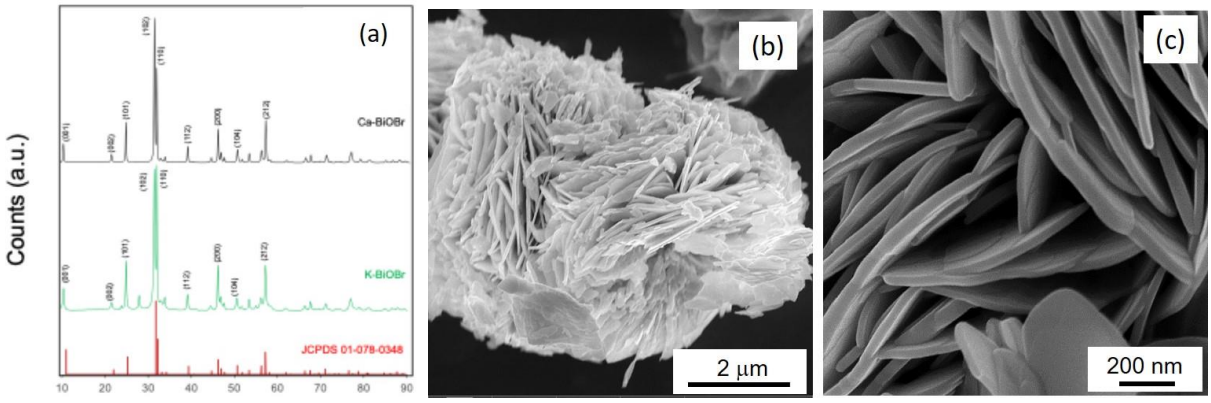
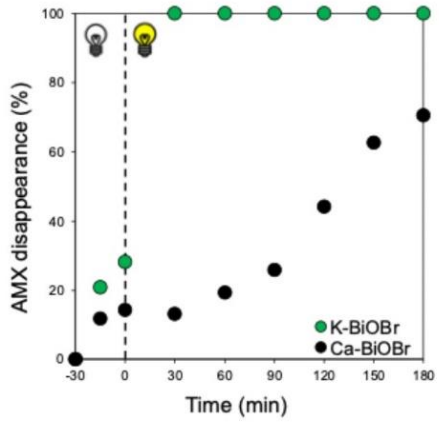


Figure 1 Section (a): XRD diffractograms of BiOBr from K (green curve) and Ca salts (black curve); sections (b) and (c): FE-SEM images at different magnification of BiOBr from Ca salt.

To check for the successful employment of these systems in photodegradation reactions, when BiOBr from K-salts was used (Figure 2), complete AMX degradation was achieved within 30 minutes of irradiation, whereas BiOBr prepared from Ca-salts showed a slower degradation, reaching about 70% AMX degradation after 180 minutes of irradiation. A similar behavior was observed with BiOCl.



In conclusion, the tunability of BiOX crystal facets offers a powerful strategy to optimize their photocatalytic activity, enhancing their effectiveness in addressing antibiotic pollution in wastewater. By harnessing sunlight, these materials show great promise for sustainable water treatment applications.

Figure 2 AMX (10 mg L^{-1}) photodegradation tests using BiOBr (0.25 g L^{-1}; different K – green dots - or Ca salts – black dots) under simulated sunlight (35 W m^{-2}).

References

1. M. Verma, A.K. Haritash, *Environmental Technology Innovation* **2020**, 20, 101072.
2. E. Falletta, M.G. Galloni, N. Mila, M. N. bin Roslan, N.A. Ghani, G. Cerrato, A. Giordana, M. Magni, S. Spriano, D.C. Boffito, C.L. Bianchi, *ACS Photonics* **2023**, 10, 11, 3929-3943.
3. H. Zhang, L. Liu, Z. Zhou, *RSC Advances* **2012**, 2, 9224-9229
4. J. Hu, X. Jing, L. Zhai, J. Guo, K. Lu, L. Mao, *Chemosphere* **2019**, 220, 77-85.

Modification of the methane dry reforming reaction mechanism during visible light illumination of the Ni/CeO_{2-x} catalyst

Kristijan LORBER[1], Janez ZAVAŠNIK[2], Jordi SANCHO-PARRAMON[3], Matej BUBAŠ[1,3], Nataša NOVAK TUŠAR[1,4] and Petar DJINOVIĆ[1,4]*

[1] National Institute of Chemistry, Hajdrihova 19, Ljubljana, Slovenia
[2] Institute Jožef Stefan, Jamova 39, Ljubljana, Slovenia
[3]Ruđer Bošković institute, Bijenička 54, Zagreb, Croatia
[4]University of Nova Gorica, Vipavska 13, Nova Gorica, Slovenia
** petar.djinovic@ki.si*

Significance and Relevance

Illumination of the nickel-ceria catalyst by visible light of about 7 sun intensity converts CH_4 and CO_2 beyond the thermodynamic equilibrium, while the energy efficiency reaches 33 %. The reaction is sustained in a purely photocatalytic mode without external heating, yielding CH_4 and CO_2 rates of 0.21 and 0.75 mmol/g_{cat}*min, respectively. This contribution analyzes the light-induced alteration of the methane dry reforming reaction mechanism and paves the road for non-thermal and highly efficient methane and CO_2 valorization under non-thermal conditions.

Preferred and 2nd choice for the topic: (1) Photocatalysis and solar energy utilization, (2) Fundamental advances in understanding catalysis
Preferred presentation: Oral only

Introduction and Motivations

Visible light-assisted conversion of CO_2 and methane into syngas (methane dry reforming reaction, DRM) over suitable (photo)catalysts is an emerging pathway for producing fuels and chemicals with minimized involvement of fossil fuels. Illumination of the catalyst enables non-thermal energy input in the form of hot carriers, thus unlocking new reaction channels. Consequently, reaction rates can be significantly accelerated, selectivity can be steered and conversions beyond the thermodynamic equilibrium can be achieved.[1,2] The DRM reaction is under thermally driven conditions troubled by fast carbon accumulation which can be overcome by nanosized (≤5nm) nickel particles. However, such small Ni entities sinter quickly under harsh reaction conditions (temperatures above 700°C). Also, the H_2/CO selectivity increases sharply as the operating temperature exceeds 700°C, which justifies the high operating temperatures. In this research, new insights into the light-driven DRM pathways were acquired, which will enable us to better understand the photocatalytic reactions and perform energy demanding chemical conversions with higher rates and selectivity under mild conditions.

Materials and Methods

The CeO_2 nanorods were synthesized according to Zabilskiy[3] and decorated with 0.5-4 wt.% of nickel. Different *in-situ* spectroscopies (UV-VIS, DRIFTS and XAS), HRTEM, XRD and wavelength- and irradiance-dependent photocatalytic experiments were performed, and the differences in the working state of the catalysts under dark and illuminated conditions were thoroughly analyzed.[4]

Results and Discussion

TEM analysis revealed the CeO_2 is in the shape of nanorods, supporting nickel particles of about 6 nm. The *in-situ* UV-Vis DRS showed that upon heating in reductive atmosphere, the bandgap values of Ni/CeO_{2-x} samples decreased more than the thermal contribution: the change is dominated by chemical change (reduction) of the catalysts (Figure 1A).

Simulation of electromagnetic properties of CeO_2 decorated with 6 nm Ni particles showed negligible absorption for wavelengths longer than 400 nm over fully oxidized CeO_2. However, partly

reduced CeO_{2-x} shows remarkable extinction in the visible part of the light spectrum. The maximum near field enhancement in the region around the contact point between Ni particle and CeO_{2-x} support is almost two orders of magnitude larger than the average value over the particle surfaces.

During photo-thermal DRM using white light, the CH_4 and CO_2 conversions were greatly increased compared to the thermo-catalytic tests at identical catalyst temperatures. In the light-assisted mode, the 2Ni catalyst produced syngas with the H_2/CO ratio of 0.61 and 0.47 at 460 and 362 °C, respectively. These values are substantially higher than the maximum values predicted by the thermodynamic equilibrium. The apparent activation energies (Ea) in the thermo-catalytic mode (90-130 kJ/mol) decreased to 30-55 kJ/mol in the light-assisted mode. The effect of wavelength on light-assisted DRM activity was tested at a constant irradiance of 300 mW cm^{-2} using different bandpass filters. The highest rate acceleration was observed between 450 - 550 nm, which correlates with the wavelength dependence of the near-field electromagnetic intensity enhancement.

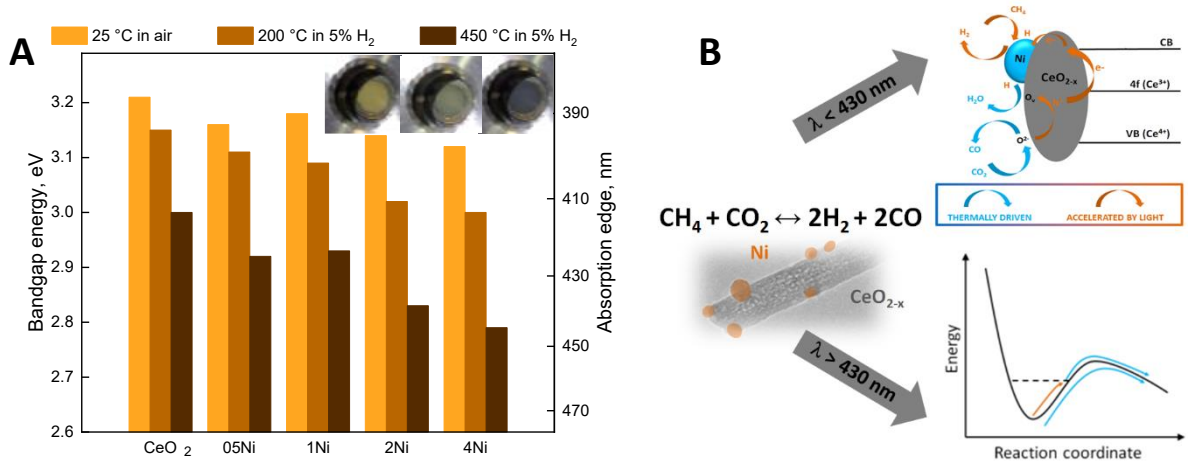


Figure 1. A) Bandgap energies for Ni/CeO_2 catalysts containing 0-4 wt. % Ni in air at 25 °C and 200 °C and 450 °C in 5 % H_2/N_2 atmosphere. Inset shows the 2Ni catalyst at mentioned temperatures and atmospheres. **B**) Proposed DRM mechanisms depending on the irradiation wavelength.

Conclusions

Based on the characterization, theoretical and photocatalytic data, we can postulate the light-assisted DRM mechanisms over Ni/CeO_{2-x} (Figure 1B).

Upon excitation with photons having energy higher than CeO_{2-x} bandgap, electron transfer from partly reduced ceria to nickel occurs, helping with C-H bond activation. Remaining hot holes on the ceria help with its re-oxidation, by incorporating oxygen from dissociated CO_2.

Upon excitation with photons having energy lower than the bandgap of ceria, the near field enhancement induces resonant and vibrational energy transfer into the Ni-CH_x bond of methane adsorbed on nickel, causing its destabilization.

References

1 K. Lorber; J. Zavašnik; J. Sancho-Parramon; M. Bubaš; M. Mazaj; P. Djinović, *Appl. Catal. B* **2022**, *301*, 120745.
2 K. Lorber; P. Djinović, *iScience* **2022**, 25, 104107.
3 M. Zabilskiy; P. Djinović; E. Tchernychova; A. Pintar, *Appl. Catal. B* **2016**, *197*, 146.
4 K. Lorber; V. Shvalya; J. Zavašnik; D. Vengust; I. Arčon; M. Huš; A. Pavlišič; J. Teržan; U. Cvelbar; B. Likozar; P. Djinović, *J. Mater. Chem. A* **2024**, 12, 19910.

Acknowledgements

Slovenian Research and Innovation agency (ARIS) is acknowledged for funding via projects N2-0265 and P1-0418.

Ti-Nb Oxide Nanotube Arrays with Cathodic Engineering for Photoelectrochemical Water Treatment and Molecular Hydrogen Production

Hyeonjeong Kim, Doyeon Kim, Eunju Hwang, Kangwoo Cho*
Pohang University of Science and Technology, Division of Environmental Science and Engineering, 77 Chungamro, Namgu, Pohang, Republic of Korea.
** kwcho1982@postech.ac.kr*

Significance and Relevance

This study comprehensively investigated the cathodization engineering on the TiO_2 nanotube array (TNA), Nb_2O_5 nanotube array (NNA), and Nb-doped TNA (Nb-TNA) for photoelectrochemical (PEC) water treatment with simultaneous energy storage into H_2. The (self-)doping mechanism depending on the cathodization conditions was tackled with thorough material characterizations. The blue-TNA, black-NNA, and Nb-TNA marked advantages under UV-, visible light-, and solar-irradiation, respectively. The results of this work would broaden the practical applicability of Ti/Nb based PEC catalysts for environmental and energy storage purposes.

Preferred and 2nd choice for the topic: Water treatment / Photocatalysis and photoelectrocatalytic approaches, solar energy utilization
Preferred presentation: Oral only

Introduction and Motivations

Amid the growing attention to the water pollution caused by recalcitrant organic micropollutants and concomitant demands on (industrial) wastewater reuse, photoelectrochemical (PEC) water treatment has been noticed as a feasible advanced oxidation process with minimal usage of chemicals with H_2 generation. Cathodization of TiO_2 nanotube array (TNA) in ambient conditions has been widely deployed to enhance the PEC) activities. Self-dopants (Ti^{3+}, intercalated H, and oxygen vacancy) or heteroatom dopants could tune the band structure, light absorbance, electrical conductivity, capacitance, and charge transfer characteristics among others. This study systematically evaluated the effects of variable cathodization conditions, including current density/duration, pH/buffering intensity of electrolyte, and sequence of annealing. This study stepped further for engineering of Nb_2O_5 nanotube array (NNA) and Nb-doped TNA (Nb-TNA) via analogous cathodization doping. The PEC activity for aqueous pollutants degradation and photocurrent generation (for H_2 generation on cathode) were comparatively evaluated. The doping mechanism was disentangled by thorough characterization based on X-ray diffraction, X-ray photoelectron/absorption spectroscopy, electron spin resonance (ESR) spectroscopy, and secondary ion mass spectroscopy.

Results and Discussion

The self-doping of anatase TNA brought about blue colored TNA, whereas the same sequence for amorphous TNA gave degenerately doped black TNA. The self-dopants were exclusively located on surface for blue TNA to improve the PEC activity for water oxidation, whereas they penetrated into bulk structure for black TNA with quasi-permanent lattice distortion to lose the PEC activity. The passed charge was more effective than the current density, whose level could be optimized by an in-situ monitoring of photocurrent. The pH and buffering intensity of electrolyte switched the levels of self-dopants on surface, owing to the doping mechanism of reductive Ti dissolution and proton intercalation. The maximal photocurrent and incident photon to current efficiency were noted in a phosphate buffer with circum-neutral pH. The cathodically modified NNA into a Black-NNA also revealed ample oxygen vacancies to elevate donor density and electrical conductivity. The band-edge shift and narrowed band gap (3.0 eV to 2.6 eV) brought about a visible light response activity of the Black-NNA. A current switching mode could overcome the chemical instability of the self-dopants under the anodic environment to elongate the lifetime. Thus, under a visible light irradiation, total amount of model aqueous pollutants degradation (under the current switching) on Black-NNTs was

39% higher than Blue-TNA. Moreover, cathodization of TNA in the presence of Nb cations effectively allowed atomic dispersion of hetero-atoms via substitutional doping. The Nb-TNA marked the supreme solar PEC activity (photocurrent), hydroxyl radical generation (as confirmed by scavenging tests, ESR, and model aqueous pollutants degradation) among the catalysts under interrogation.

Consequently, relatively simple electrochemically self-doping was confirmed to be a viable way for the engineering of TNA, NNA, and hybrids to be utilized for PEC water treatment. The hydroxyl (OH) radical by water oxidation on the PEC catalysts could be utilized for degradation of non-biodegradable organic compound (poly-acrylic acid, aromatic micropollutants among others) for water reuse. In addition, the OH radical driven chlorine evolution reaction can mediate breakpoint chlorination of aqueous ammonia as a pollutant. Simultaneous conversion of solar energy into molecular hydrogen can be a sustainable approach towards water-energy nexus. The results of this study would broaden the usage of TiO_x and NbO_x nanomaterials by engineering the physico-chemical properties depending on variable energy input and application scenarios.

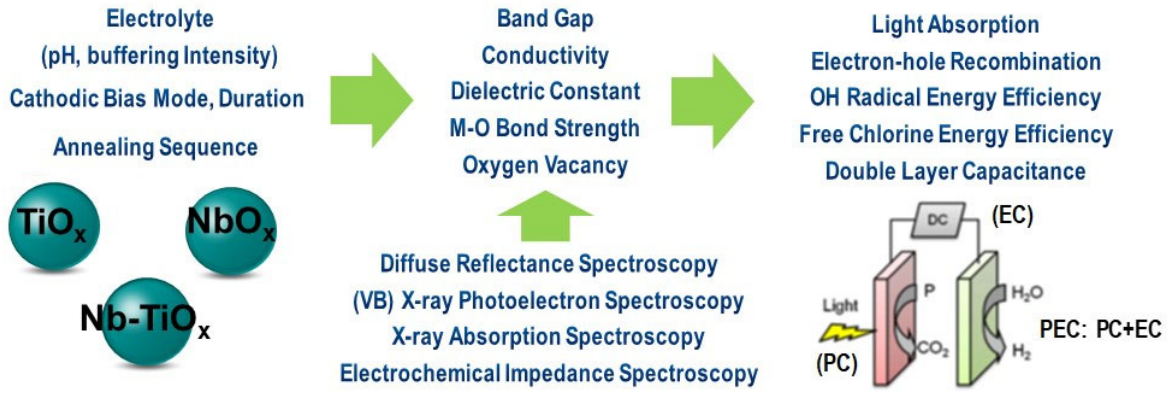


Figure 1. Outline of the research scope

Flux Synthesis of Layered Perovskite Oxyiodide Photocatalyst for Visible-Light-Driven Water Splitting

Makoto OGAWA[1], Hajime SUZUKI[1], Kanta OGAWA[1], Hiroki UBUKATA[1], Osamu TOMITA[1], Akinobu NAKADA[1], Shunsuke NOZAWA[2], Akinori SAEKI[3], Hiroshi KAGEYAMA[1], Ryu ABE[*,1]

[1] *Kyoto University, Grad. Sch. of Eng., Kyoto daigaku-katsura, Nishikyo-ku, Kyoto, Japan.*

[2] *Photon Factory (PF), Institute of Materials Structure Science (IMSS), High Energy Accelerator Research Organization (KEK), Tsukuba, Ibaraki 305-0801, Japan.*

[3] *Department of Applied Chemistry, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan.*

** ryu-abe@scl.kyoto-u.ac.jp*

Significance and Relevance

We report a novel solution-based synthetic approach, the flux method, for the Sillén–Aurivillius layered perovskite oxyiodide Bi_4NbO_8I. The flux method provides well-crystalized plate-like particles, improving charge carrier transport property and photocatalytic water oxidation activity compared to the sample prepared via the conventional solid-state reaction (SSR). Surface modification further exploits the flux sample's superior bulk property, achieving an apparent quantum efficiency (AQE) of 8.8% for sacrificial O_2 evolution at 405 nm, the highest value reported for oxyiodide photocatalysts.

Preferred and 2nd choice for the topic: "Photocatalysis and photoelectrocatalytic approaches, solar energy utilization" preferred or "H_2 storage and transportation, green H_2 production, hydrogen vectors"
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Sillén–Aurivillius layered perovskite oxyiodides, such as Bi_4NbO_8I, have recently emerged as a new class of materials for visible-light-driven water splitting photocatalysis, owing to their narrow band gaps and high photocatalytic activities.[1–3] However, their synthesis has been limited to conventional SSR, hindering us from fully exploiting the material's potential.

Results and Discussion

Bi_4NbO_8I (Figure 1) samples were synthesized using both the conventional SSR method and the flux method, with Bi_3NbO_7 and BiOI as precursors. For the flux synthesis, we employed an alkali metal iodide (eutectic mixtures of CsI and KI) as a molten salt to create an I-rich environment. Chloride salts used as a flux resulted in the chloride counterpart, Bi_4NbO_8Cl, even with BiOI used as a precursor, highlighting the necessity of an iodide-based flux to maintain I-rich conditions. After calcining the precursor with the molten salt in an evacuated quartz tube, the salts were washed away to obtain the product.

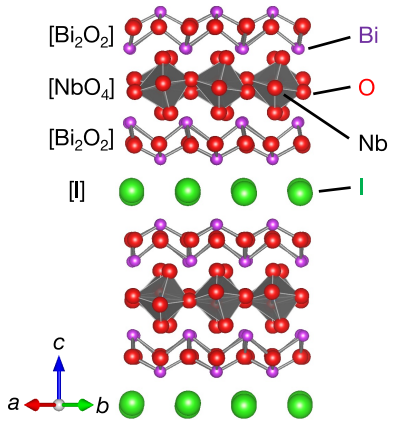


Figure 1 Crystal structure of Sillén–Aurivillus phase Bi_4NbO_8I.

While the SSR sample consists of an agglomeration of irregularly shaped particles (Figure 2a), the flux synthesis resulted in plate-like particles (Figure 2b). In addition, the product exhibits a single-crystalline nature, as revealed by the transmission electron microscopy (TEM) image and the corresponding selected area electron diffraction (SAED) patterns (Figures 2c and 2d).

The band gap of Bi_4NbO_8I samples prepared using the flux method was estimated to be 2.45 eV from the absorption edge of 506 nm, identical to that of the SSR sample.[3] The dynamics of photogenerated carriers in Bi_4NbO_8I were investigated by time-resolved microwave conductivity (TRMC) measurement.[4] The TRMC signal corresponds to the product ($\varphi\sum\mu$) of the charge carrier generation efficiency φ and the sum of charge carrier mobilities $\sum\mu$, and the decay profile reflects the carrier lifetime. The flux sample exhibited over three times higher intensity and a longer carrier half-

lifetime ($\tau_{1/2}$) than that of the SSR sample (Figure 3a). These results show that the flux sample is superior in carrier transport properties to the SSR one, which can be attributed to its high crystallinity (Figure 2d).

Photocatalytic water oxidation activity was investigated in the presence of an electron acceptor (Ag^+). As shown in Figure 3b, the optimized IrO_x-loaded flux sample presented a superior activity to that of the SSR one. The enhanced carrier transport properties of the flux-synthesized sample (Figure 3a), along with its higher surface area (Figures 2a and 2b), can be the improvement factors. The AQE for sacrificial O_2 evolution reached 8.8% at 405 nm, which is the best-reported performance for oxyiodides. Moreover, we demonstrated the visible-light Z-scheme water splitting using Bi_4NbO_8I as an O_2 evolution photocatalyst (Figure 3c).

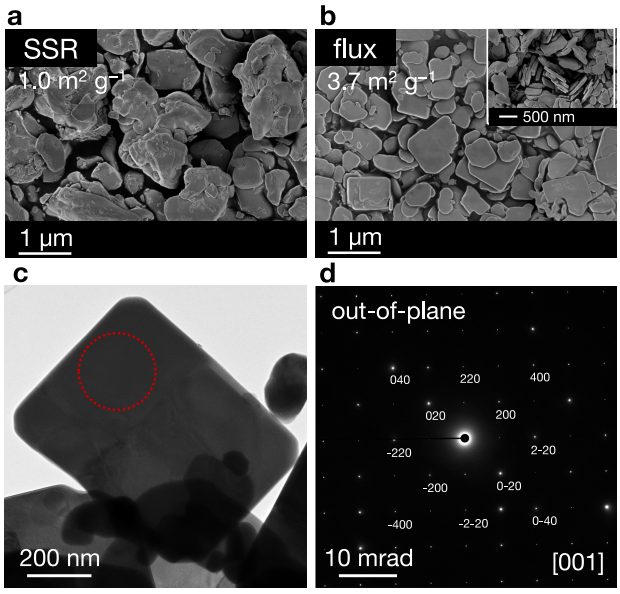


Figure 2 SEM images of Bi_4NbO_8I samples prepared via (a) the flux method and (b) SSR method. (c) TEM image, and (d) the corresponding SAED pattern of the flux-synthesized sample.

The present synthetic method for oxyiodides and the provided high-quality microcrystalline particles offer a useful playground for designing and modifying the particles for more efficient water-splitting. We also believe that this flux synthesis approach is applicable to a variety of functional iodine-based materials, including other Sillén–Aurivillius phases, paving the way for oxyiodides as high-performance functional materials.

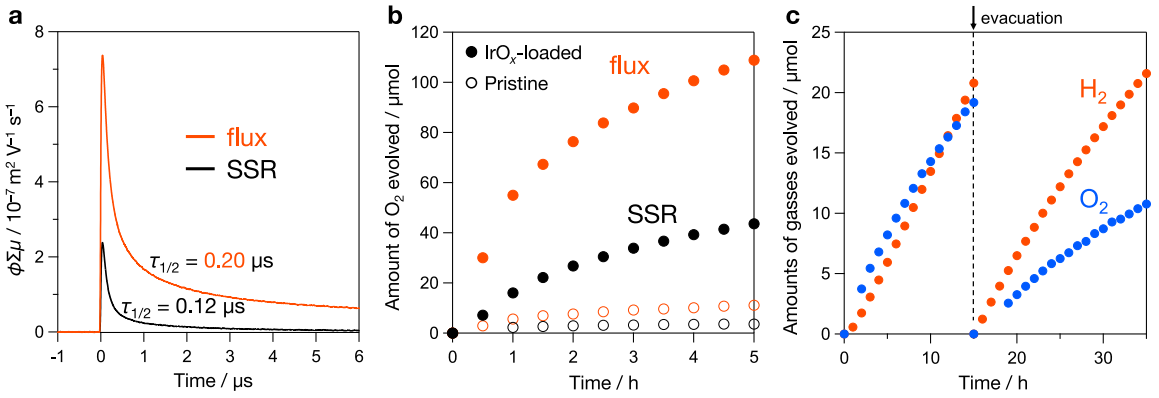


Figure 3 (a) TRMC transient decay profiles of pristine Bi_4NbO_8I samples prepared via the flux method and SSR method. (b) Time courses of O_2 evolution over pristine and IrO_x-loaded Bi_4NbO_8I samples prepared via the flux method and SSR method in an aqueous $AgNO_3$ solution under visible light irradiation. (c) Time courses of H_2 and O_2 evolution over a mixture of $RuO_x/SrTiO_3$:Rh and $IrO_x/(Fe,Ru)O_x/Bi_4NbO_8I$ in an aqueous $Fe(NO_3)_3$ solution under visible light irradiation.

References

1. K. Ogawa, H. Kageyama, R. Abe et al., *J. Am. Chem. Soc.* **2021**, *143*, 8446−8453.
2. M. Ogawa, R. Abe et al., *Solid State Sci.* **2023**, *141*, 107221.
3. K. Ogawa, A. Walsh, R. Abe et al., *Chem. Mater.* **2023**, *35*, 5532−5540.
4. H. Suzuki, R. Abe, A. Saeki et al., *ACS Energy Lett.* **2019**, *4*, 1572−1578.

Acknowledgements

This work was supported by the JSPS KAKENHI Grant Numbers JP20H00398, JP23H02061, and JP24KJ1470, and the JSPS Core-to-Core Program (JPJSCCA20200004).

Squeezing Water Molecular Network with Kosmotropic Chemistry to Enhance Nitrogen-to-Ammonia Electrofixation

Jiajia Zhang[1], Zhi Zhong Ang[1], Hiang Kwee Lee[*,1,2,3]

[1] *Division of Chemistry and Biological Chemistry, School of Chemistry, Chemical Engineering and Biotechnology, Nanyang Technological University, 21 Nanyang Link, Singapore 637371, Singapore.*

[2] *Institute of Materials Research and Engineering, The Agency for Science, Technology and Research (A*STAR), 2 Fusionopolis Way, #08-03, Innovis, 138634, Singapore.*

[3] *Centre for Hydrogen Innovations, National University of Singapore, E8, 1 Engineering drive 3, 117580, Singapore.*

** e-mail corresponding: hiangkwee@ntu.edu.sg (Hiang Kwee Lee)*

Significance and Relevance

The electrochemical nitrogen reduction reaction (NRR) is promising for green ammonia production due to its mild operation conditions but still facing challenges like low solubility and inertness of nitrogen (N_2) and the competing hydrogenation process between hydrogen evolution reaction (HER) and NRR. By squeezing the water molecular network at the point-of-catalysis, our work offers a unique perspective to chemically enhance electrochemical NRR and modulate catalytic pathways. We envision advancements in both functional surface chemistry and efficient electrocatalytic materials are jointly critical to accelerate progress towards green ammonia production in sustainable energy and chemical applications.

Preferred and 2nd choice for the topic: Fundamental advances in understanding catalysis; Multiscale modeling and advanced simulation aspects

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Ammonia plays a crucial role in modern civilization as a nitrogen precursor, but current ammonia production relies mainly on the harsh Haber-Bosch process (200 atm, 500°C) [1,2]. To enable sustainable urbanization and industrialization, immense research efforts have thus focused on developing greener nitrogen fixation methods for ammonia production [3-5]. The electrochemical NRR is promising for green ammonia production due to its use of milder proton sources (e.g., water), ambient operation conditions, and facile integration with renewable electrical energy [6-8]. However, achieving efficient NRR remains a formidable challenge due to the high stability of the N≡N triple bond. Additionally, the electrochemical HER competes strongly with NRR because the two-electron HER process is kinetically favored over the six-electron NRR [9,10]. Herein, we enhance electrochemical NRR by functionalizing electrocatalyst surfaces with hydrophilic molecules that impart unique kosmotropic chemistry to control water molecules near the catalytic sites. This kosmotropic chemistry strengthens water-water intermolecular hydrogen bonding to expel N_2 molecules from the water network, thereby facilitating their approach towards and interaction with the electrocatalytic sites for promoting NRR. Our work's novelty thus lies in regulating the local water microenvironment to promote NRR, distinct from conventional hydrophobic surface modifications that deter water molecules from the electrocatalyst.

Materials and Methods

We begin by synthesizing nanoporous gold bowls (NPGB) catalysts through a two-step, seed-mediated method. This process involves the initial synthesis of AgCl nanocube as sacrificial template with poly(vinyl pyrrolidone) (PVP) serving as surfactant, followed by growth of NPGBs onto the AgCl templates and subsequent chemical etching of AgCl template. The as-synthesized NPGBs exhibit a gyri-like morphology, comprising bowl-like structures with uniformly interdigitated ligaments. We subsequently functionalize the NPGB surfaces with five different para-substituted aromatic thiols to impart kosmotropic or chaotropic surface chemistries, leveraging the strong affinity of thiol moieties with gold. We confirm the successful modification of NPGB with these thiol molecules through XPS and SERS characterizations.

Results and Discussion

Based on our NPGBs electrocatalyst, we demonstrate that kosmotropic chemistry is crucial for boosting NRR among the five surface chemistries investigated. Notably, our best-performing kosmotropic electrocatalyst (BTP-modified NPGBs) achieves superior NH_3 yield rate and Faradaic efficiency, with over 16-fold and 20-fold improvements compared to chaotropic counterparts, respectively. These enhancements can be infinitely superior considering that the most chaotropic NPGB yields no ammonia. Mechanistic investigations reveal that kosmotropic molecules strengthen hydrogen bonding among water molecules, creating a tightly bound water molecular network that readily expels N_2 reactants from the water matrix. This phenomenon is crucial for promoting catalyst-N_2 interactions and kinetically boosting NRR while suppressing HER.

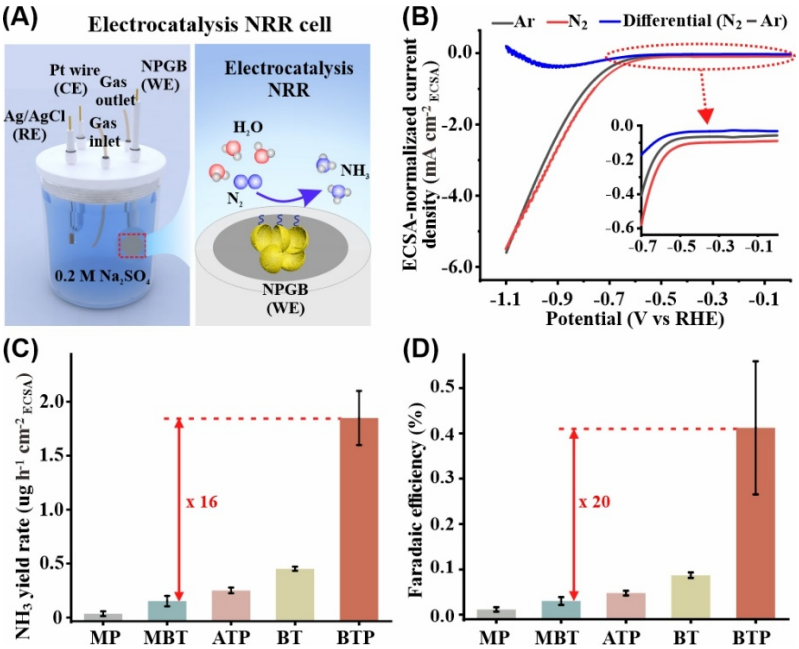


Figure 1. (A) Schematic of the electrochemical cell for NRR using various surface-modified NPGBs as the electrocatalysts. (B) Linear sweep voltammograms (LSV) recorded from BTP-modified NPGBs under N_2 or Ar bubbling. Insert, a magnified LSV plot between 0 and -0.7 V. (C) Electrochemical NH_3 yield rate and (D) corresponding Faradaic efficiency of various thiol-modified NPGBs at -0.3 V vs RHE.

References

1. B. H. R. Suryanto, H. Du, D. Wang et al. Nature Catalysis, 2 (2019) 290-296.
2. L. Wang, M. Xia, H. Wang et al. Joule, 2 (2018) 1055–107.
3. J. G. Chen, R. M. Crooks, L. C. Seefeldt et al. Science, 360 (2018) 873.
4. H. L. Du, M. Chatti, R. Y. Hodgetts et al. Nature, 609 (2022) 722–727.
5. O. Westhead, J. Barrio, A. Bagger et al. Nature Reviews Chemistry, 7 (2023) 184–201.
6. G. Soloveichik. Nature Catalysis, 2(2019) 377-380.
7. X. Zhao, G. Hu, G. Chen et al. Adv. Mater. 33 (2021) 2007650.
8. B. Yang, W. Ding, H. Zhang, S. Zhang. Energy Environ. Sci. 14 (2021) 672.
9. X. Zhang, X. Zhu, S. Bo, C. Chen et al. Chem, 10 (2024) 1516–1527.
10. H. Zhang, H. Wang, X. Cao et al. Adv. Mater. 36 (2024) 2312746.

Acknowledgements

H.K.L. thanks the funding supports from Singapore Ministry of Education (AcRF Tier 1 RS13/20 and RG4/21), A*STAR Singapore (MTC IRG M23M6c0098 and AME YIRG A2084c0158), National University of Singapore Center of Hydrogen Innovation (CHI-P2022-05), and Nanyang Technological University start-up grants. The research was conducted as a part of NICES (NTU-IMRE Chemistry Lab for Eco Sustainability; REQ0275931), a joint research initiative between Nanyang Technological University (NTU) and Institute of Materials Research and Engineering (IMRE) from Agency for Science, Technology and Research (A*STAR).

Photocatalysts and essential oils: could they ever be friends?

Andrea CAMPOSTRINI[1,2], Teresa BOTRE'[1,2], Sabrina MANENTE[1], Pilar BOSCH-ROIG[3], Elena GHEDINI[4], Michela SIGNORETTO[1,2], Federica MENEGAZZO[*,1,2]

[1]*Ca' Foscari University of Venice, Department of Molecular Sciences and Nanosystems, Via Torino 155, 30172 Venice, Italy.*

[2]*INSTM RUVe, Via Torino 155, 30172 Venice, Italy.*

[3]*Universitat Politècnica de València, Instituto Universitario de Restauración del Patrimonio, Camí de Vera s/n, 46022 Valencia, Spain.*

[4] *University of Bari, Chemistry Department, Via Orabona 4, 70126 Bari, Italy.*

**federica.menegazzo@unive.it*

Significance and Relevance

The combination of photocatalysts and essential oils, both encapsulated on mesoporous silica, was tested as the main component of a protective coating for stone and cementitious surfaces. The promising synergic results showed that this system could be of interest for inhibiting and preventing microbiological growth on such surfaces, while also avoiding visible aesthetic impacts or color changes, being non-toxic for the environment or the operator, and increasing the duration of the antimicrobial effect, thus preventing future colonization by threatening microorganisms.

Preferred choice for the topic: Photocatalysis and photoelectrocatalytic approaches, solar energy utilization
Preferred presentation: (Oral)

Introduction and Motivations

Even though stone and cementitious surfaces might seem made of very resistant materials, they still undergo several degradation phenomena, which are strictly related to the environment they are exposed to. These phenomena can derive from different sources: chemical, physical-mechanical, or biological. In the latter case, it is referred to as biodeterioration. To avoid such degradation phenomenon, preventive actions must be considered, such as the application of antimicrobial protective coatings.[1]

This work presents a green nanostructured system aimed at developing a protective coating for stone and cementitious surfaces exposed outdoors. Currently, most antimicrobial products used to contrast microbiological growth are highly toxic not only for the target organisms but also for the operators and the environment. For this reason, attention must be given to employing sustainable alternatives. In this regard, the use of essential oils (EOs) has emerged. EOs have a high antimicrobial power; however, their action is often time-limited and regulated by the evaporation time of the active molecules. To increase the duration of the antimicrobial effect, we have investigated the possibility of adding a photocatalyst to the coatings, in which EOs-impregnated silica had already been incorporated. The presence of a photocatalyst in the mixture would not only prolong the biocide effect, but also ensure air pollutants abatement and a self-cleaning effect on the stone surface. However, the question raised: photocatalysts and EOs would act in conflict or cooperate in a synergistic action?

Materials and Methods

The silica mesoporous material MCM-41 was synthesized and employed as a nanocontainer to host and subsequently release antimicrobial products such as EOs (i.e., *Origanum Compactum* and *Thymus Vulgaris*).[2] Furthermore, the system was enriched by adding different titanium dioxide photocatalysts (Degussa P25, Mirkat 211, and Kronos VLP), varying in size and crystalline phase. These enriched nano capsules were incorporated into a hydrogel for the formulation of the coating. A hybrid hydrogel was chosen, employing chitosan bio-polymer as organic component and silica precursors methyltriethoxysilane (MTES) and tetraethylorthosilicate (TEOS) as inorganic components. To evaluate photocatalytic activity, tests on different mock-ups (e.g. Carrara and Serpentine marbles, plaster, Serena stone, …) were carried out, simulating organic deposition using Methylene Blue as a model

stain compound. *In vitro* microbiological tests were conducted on two Fungi (*Aspergillus niger* and *Penicillium rubens*), taken as model microorganisms from real-case scenarios.

Results and Discussion

First, two EOs (namely *Origanum Compactum* or *Thymus Vulgaris*) were encapsulated in MCM-41. This ensures that the antimicrobial features of EOs are maintained for a longer duration, reducing the evaporation rate and diminishing the quantity required: the amount necessary to achieve the minimum inhibitory concentration (MIC) and the minimum fungicidal concentration (MFC) was halved. Moreover, since the silica can host a higher quantity of products than is necessary to exert the antimicrobial effect, the duration of activity is prolonged, releasing the EOs over time. This combination of mesoporous silica and EOs was tested as the principal component of a protective coating for stone surfaces. The promising synergic results show that this system could be of interest for inhibiting and preventing microbiological growth on stone surfaces, while also avoiding visible aesthetic impacts or color changes, being non-toxic for the environment or the operator, and preventing the EOs from evaporating holding them for gradual release.

Furthermore, the system was enriched by adding titanium dioxide (TiO_2) photocatalysts (Degussa P25, Mirkat 211, or Kronos VLP) to increase the duration of the antimicrobial effect, thus preventing future colonization by threatening microorganisms. In addition, the presence of a photocatalyst in the mixture would ensure air pollutants abatement, such as NOx and VOCs, and a correlated self-cleaning effect on the surface. For the development of the protective coating, a two-step impregnation process was used. First, MCM-41 was impregnated with EO to ensure its penetration to the silica pores. Titania was added afterwards to ensure it remained on the surface, providing sites for its photocatalytic activity. The latter was tested in the degradation of methylene blue, used as a model stain compound. The essential oil-impregnated silica particles enriched with titania proved to be effective. The best results were obtained with the material containing Degussa P25. This result was correlated to the appropriate band gap and to the combination of rutile and anatase crystalline phases of the sample.

Finally, this multifunctional material was incorporated into a hydrogel for the formulation of the coating. The formulation was then applied to stone and cementitious mock-ups to evaluate its hydrophobic and colorimetric properties. The newly formulated coating proved to be highly effective, as it did not alter the morphology or color of the substrate. Additionally, it significantly improved the hydrophobic properties of the mock-ups.

The antimicrobial activity of the coating was tested using two Fungi (*Aspergillus niger* and *Penicillium rubens*), taken as model microorganisms from real-case scenarios. The results highlight the potential of mesoporous MCM-41 silica encapsulating both vegetal extracts and photocatalysts as a sustainable and effective solution for inhibiting microbiological growth on stone and cementitious surfaces. The promising synergic results showed that this system could be of interest not only for inhibiting and preventing microbiological growth on stone surfaces, but also for avoiding visible aesthetic impacts or color changes, being non-toxic for the environment or the operator, and increasing the duration of the antimicrobial effect, thus preventing future colonization by threatening microorganisms.

Future studies will focus on evaluating the shelf life of the product, since understanding how long the coating remains effective under various storage conditions is crucial.

References

1. F. Bartoli, *et al.*, *Coatings* **2024**, *14 (2)*, 163.
2. A. Campostrini, *et al.*, *Next Materials* **2025**, *7*.

Acknowledgements

“PON Ricerca e Innovazione 2014–2020”, “Fondo per la promozione e lo sviluppo delle politiche del Programma Nazionale per la Ricerca (PNR) 2021–2027”, and the restoration company Uni.S.Ve. S.r.l. of Venice (Italy) are acknowledged.

Novel application of CuMg-based Layered Double Hydroxides as photocathodes for photoelectrocatalytic CO_2 conversion

Eleonora TOSI BRANDI[*1], *Andrea FASOLINI*[1], *Jacopo DE MARON*[1], *Nicola SANGIORGI*[2], *Alex SANGIORGI*[2], *Alessandra SANSON*[2], *Francesco BASILE*[1]

[1] *University of Bologna, Industrial Chemistry Department, Viale del Risorgimento 4, 40136, Bologna, Italy.*

[2] *National Research Council of Italy, Institute of Science, Technology and Sustainability for Ceramics (CNR-ISSMC), Via Granarolo 64, 48018, Faenza, Italy.*

**eleonora.tosibrandi2@unibo.it*

Significance and Relevance

The photoelectrocatalytic reduction of carbon dioxide (CO_2RR) to generate valuable fuels and chemicals using renewable energy is a promising approach to convert intermittent green energy sources into chemical energy, decrease our reliance on fossil fuels, and simultaneously lower net carbon dioxide emissions. Herein, the authors propose for the first time the application of Cu-based LDH as photocathode's material for simultaneous light-absorption and CO_2 catalytic conversion into C_2 and C_3 oxygenated products such as acetic acid, ethanol, and 1-propanol.

Preferred and 2nd choice for the topic: 1) Photocatalysis and photoelectrocatalytic approaches, solar energy utilization; 2) CO2 utilization and recycling
Preferred presentation: Oral preferred

Introduction and Motivations

Photoelectrocatalysis is an innovative and sustainable approach to drive chemical transformations using renewable energy. Simultaneously, the valorization of CO_2 has gained significant attention due to its potential as a sustainable strategy to mitigate atmospheric greenhouse gas concentrations while serving as a resource for fuel and chemical production. Significant progress has been made in identifying optimal materials for efficient CO_2 reduction reactions (CO_2RR) in photoelectrocatalytic systems. [1] Layered Double Hydroxides (LDHs), a class of anionic clays, are particularly promising for this application due to their strong affinity for CO_2 and their tunable chemical composition. [2,3] This versatility enables the modification of their morphological, physicochemical, and electrochemical properties to enhance light absorption and catalytic efficiency. This study explores the synthesis, characterization, and catalytic performance of Cu-based LDHs as catalysts in photoelectrochemical cells (PECs), with a focus on the active phases and CO_2 interaction properties inherent to these tailored materials.

Results and Discussion

Two LDH compositions were investigated i.e. CuMgAl, CuMgFe with M(II)/M(III) ratio equal to 3. XRD and SEM analysis underlined the morphological homogeneity of the samples, both powder and films, as well as the presence of the desired LDH phase. Band gap and electronic energy levels' position of the samples have been defined and confirmed compatible with standard potentials of CO_2RR thanks to UV-vis DRS and Mott-Schottky analysis respectively. These materials are characterized by a film band gap between 2.20 and 2.90 eV and showed a p-type semiconductor behavior. The characterization of the electron transfer ability, charge accumulation capability, materials conductivity, and photocurrent generation capacity of the samples by CV, EIS and LSV confirmed the suitability of these materials to be employed as photoelectrodes.

XRD, SEM-EDX characterizations were also performed on spent catalysts to assess materials transformation phenomena occurred during the reaction.

These properties were linked to photoelectrocatalytic activity. Indeed, the investigated compositions demonstrated to be active in photoelectrochemical CO_2RR with higher selectivity for C-containing products i.e., acetic acid and formic as major products and other minor products such ethanol over

hydrogen evolution at relatively low potential of – 0.4 V vs RHE, while H_2 production was the favored when higher potential was applied i.e., – 0.9 V vs RHE.

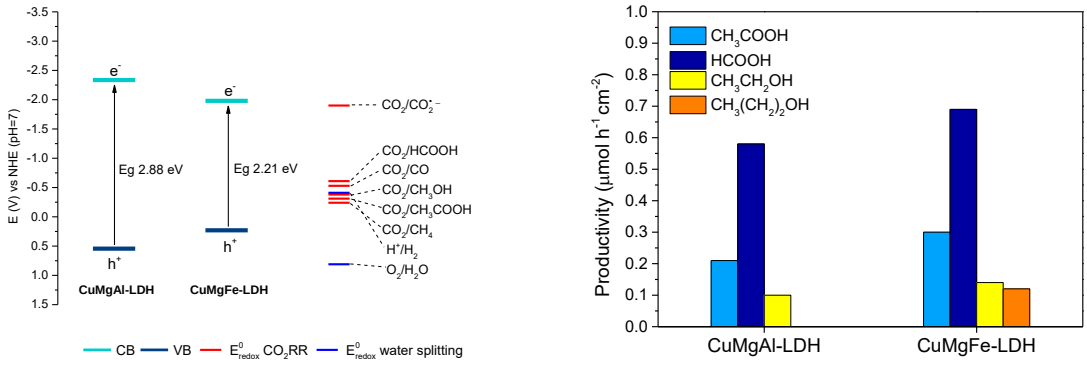


Figure 2 - Experimentally determined conduction and valence band edges and thermodynamic redox potentials of CO_2 reduction products on a potential diagram, depicting favorable energetics for photo-assisted CO_2 reduction (left). Photoelectrochemical CO_2RR liquid products obtained after 1 h at -0.4 V vs RHE in 0.3 M $KHCO_3$ electrolyte solution (right).

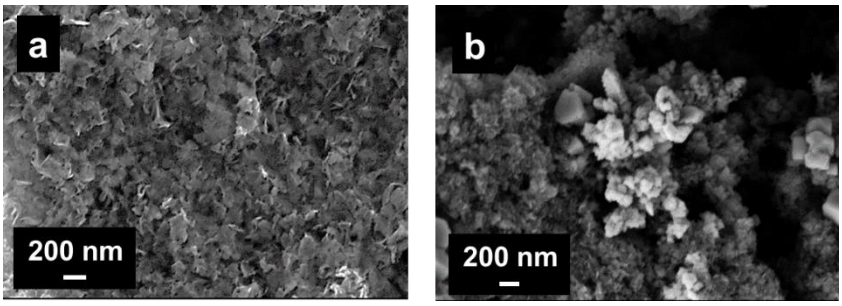


Figure 1 – High magnification FE-SEM images of spent photocathodes: a) CuMgAl-LDH film still presenting lamellar morphology; b) nanostructures formed on CuMgFe-LDH film.

Fe-containing LDH has been found to be the most active for CO_2 conversion to acetic acid under an applied potential of - 0.4V vs RHE (J_{reac} = 1 mA cm^{-2}) and able to produce also a C_3 product such as 1-propanol. Therefore, the synergistic effect between Fe and Cu in the LDH structure facilitated the creation of active sites (i.e. Cu_2O/Cu^0) essential for catalyzing the reduction of CO_2 which are in intimate contact with a CO_2 absorption phase (i.e. LDH). These results disclose the potential application of this class of materials for solar fuels production.

References

1. J. He, C. Janáky, ACS Energy Lett., 2020, 5, 1996–2014.
2. D. Chaillot, S. Bennici, J. Brendlé, Environ. Sci. Pollut. Res., 2021, 28, 24375–24405.
3. M. Serafini, F. Mariani, A. Fasolini, E.T. Brandi, E. Scavetta, F. Basile, D. Tonelli, Adv. Funct. Mater., 2023, 33, 2300345.

Acknowledgements

Part of this work was financed by the European Union - NextGenerationEU through the Italian Ministry of University and Research under PNRR “Piano Nazionale di Ripresa e Resilienza” - Mission 4 “Istruzione e Ricerca” Component 2 “Dalla ricerca all’impresa”, Investment 1.1, “Fondo per il Programma Nazionale di Ricerca e Progetti di Rilevante Interesse Nazionale (PRIN) – Piano Nazionale di Ripresa e Resilienza, addressed to Progetti di Ricerca di Rilevante Interesse Nazionale”. D.D. n. 104 del 2/2/2022, Project title: CO_2 COnversion to REnewable fuels by dynamic Adsorption and Transformation on LAyered Structured based catalysts - CO_2
CORE AT LAST, Code 2022MPEXJW, CUP J53D23007640006

Solar-driven CO_2 electroreduction with direct-coupled PV-EC in realistic operating cycles

Tsvetelina MERDZHANOVA*[1], Thérèse CIBAKA[1], Oleksandr ASTAKHOV[1]
[1] *IMD3-Photovoltaics, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany*
** e-mail corresponding: t.merdzhanova@fz-juelich.de*

Significance and Relevance

In this work we design, and test direct-coupled PV-EC device for converting CO_2 into chemical products with emulated PV devices reproducing IV characteristics of real PV modules in the field at most relevant irradiance/temperature combinations with precision and accuracy on par with class A+ solar simulator [1]. The emulated PV of the PV-EC device can be adjusted to the required size of the lab scale EC cell used for CO_2 electroreduction. PV emulation offers stable operation of the PV-EC system over diurnal cycles allowing to establish correlation between performance, coupling factor and solar-to-fuel efficiency. This is of importance for future improvements of the electrical design of such systems and their performance in realistic cycles.

Preferred and 2nd choice for the topic: Photocatalysis and photoelectrocatalytic approaches, solar energy utilization
Preferred presentation: (Oral only)

Introduction and Motivations

The rising levels of CO_2 in the atmosphere require the development of novel approaches to carbon management. Moreover, the installed capacity of photovoltaic (PV) systems is expanding at a considerable rate, resulting in a significant discrepancy between the generation of electricity from PV sources and the actual demand for electricity. The long-term storage of energy in molecules such as fuels or other industrially useful chemicals is of particular significance in counterbalancing the seasonal variations in photovoltaic power generation. The direct-coupled photovoltaic-electrochemical (PV-EC) system addresses these issues by converting excess PV energy into chemicals prior to feeding it to the grid. This enhances the utilization of photovoltaic power and improves grid stability.

Materials and Methods

In this study, we have designed and tested a direct-coupled photovoltaic (PV) electrocatalytic (EC) device for the conversion of carbon dioxide (CO_2) into carbon monoxide (CO) and hydrogen (H_2) (see Figure 1). The device employs emulated PV that reproduces the IV characteristics of real PV modules in the field at the most relevant irradiance and temperature combinations (Figure 1(a)). The characteristic operating points of the PV-EC were obtained using the NREL public database for silicon heterojunction (SHJ) modules installed in specific regions of the USA. The newly developed PV emulator routine enables the precise and accurate reproduction of any IV characteristic of a PV module, at a level comparable to that of a Class A+ solar simulator [2]. In our study, a SHJ module with an emulated area of 44.5cm² drives a flow-type stack EC cell (area 9.5cm²) with a silver/gas diffusion layer (GDL) cathode [3] and an iridium oxide anode (see Figure 1(b)).

Results and Discussion

The operation of the PV-EC system was evaluated under dynamic conditions, represented by three sunny days in a cycling procedure. This procedure involved eleven steps of irradiance-temperature pairs, ranging from 0.2 Sun to 1.1 Sun and 20°C to 54°C, followed by idle 'night' periods (see Figure 2(a)). The operating voltages achieved were in the range of 2.4 to 3.2V, while the operating currents were between 70 and 335mA corresponding to current densities of 7.4 to 35.2mA/cm^2 (see Figure 2(b)). The solar-to-chemical efficiency was observed to range between 8.7 and 10.8% at a high degree of coupling (0.85 to 1) in the absence of power electronics. Finally, a consistent and stable dynamic operation towards CO as the primary product with 75% faradaic efficiency and H_2 (25%) as a by-product over one to three-day cycles was demonstrated. This coupling, in conjunction with the high selectivity

towards CO, renders the approach an attractive one for the decentralized storage of excess PV energy, offering a material-saving route.

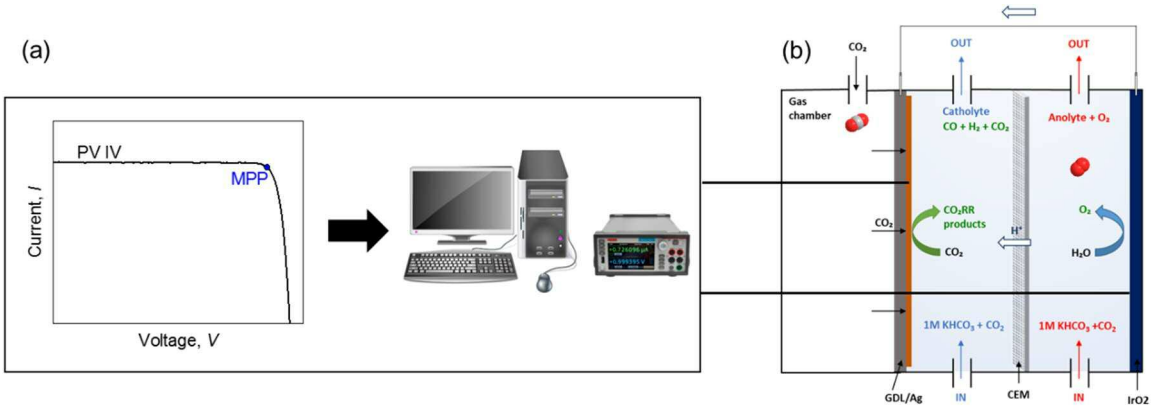


Figure 1 (a) PV emulation is realized with a custom PYTHON script controlling a standard source measure unit (SMU), whereby the emulator program takes the IV characteristics of the PV device of interest and controls the SMU output to reproduce the behavior of the PV device at the terminals of the SMU. (b) An EC cell with a gas chamber next to Ag/GDL electrode and 2 electrode chambers separated by a cation exchange membrane CEM (Nafion N117, thickness 0.007 inch) and a 1M KHCO3 electrolyte saturated with CO_2 (20 cm^3min^{-1}) flowing in both chambers. Both devices are in direct connection without power electronics in between.

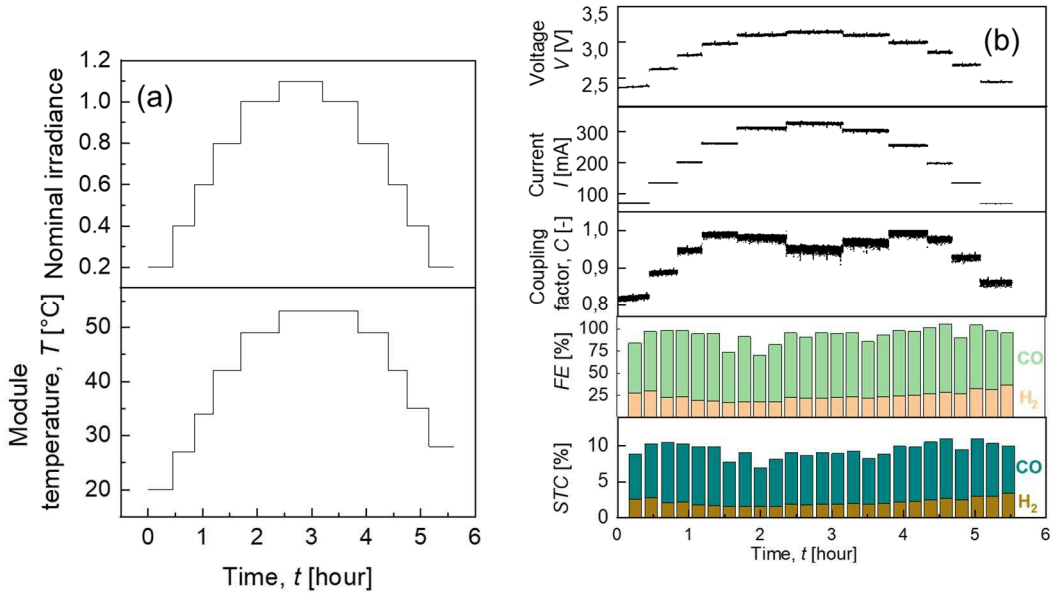


Figure 2 (a) Time profile of a summer day realized on shorter timescale with 16 hours of real time emulated in 5 hours of experiment. (b) Voltage, current, coupling factor, Faradaic efficiency and solar-to-chemical efficiency of the PV-EC investigated over 5 hours of dynamic operation.

References

1. T. Cibaka et al., *Energy Env. Sci.*, 2024 submitted.
2. B. P. M. F. Seidler et al., *J Power Sources,* 2024, under review.
3. G. Liu et al., *Chemical Engineering Journal* 2023, 40, 141757.

Acknowledgements

The authors gratefully acknowledge the European Commission under the DECADE Project (Grant agreement no: 862030).

A new double dielectric barrier discharge (DDBD) reactor to prevent carbon deposition in plasma-assisted non-oxidative methane coupling

Victor LONGO[1*], Luana DE PASQUALE[1], Siglinda PERATHONER[1], Gabriele CENTI[1], Chiara GENOVESE[1]
[1]*University of Messina, Dept. of Chemical, Biological, Pharmaceutical and Environmental Sciences and CASPE INSTM, Viale F.S. D'Alcontres 31, Messina, Italy.*
* victor.longo@studenti.unime.it

Significance and Relevance

An alternative plasma double dielectric barrier discharge (DDBD) reactor utilizing water as the ground electrode is proposed to prevent coke formation in the anaerobic methane upgrading. This approach achieves nearly 100% selectivity for alkanes using a micrometric gap (0.5 mm) while ensuring long-term stability, offering an effective solution for electrified and clean methane upgrading.

Preferred and 2nd choice for the topic:

- *Preferred:* **Advanced process with electrocatalysis and plasma utilization**
- *2nd choice:* **Catalysis to electrify the chemical production**

Preferred presentation: **Oral preferred or Short Oral / Poster**

Introduction and Motivations

The non-oxidative conversion of methane (NOCM) is a dream reaction to directly convert methane into higher hydrocarbons to avoid the formation of oxygenate intermediates or undesired CO_2. Nevertheless, the controlled and selective activation of the C-H bond(s) represents a major challenge, to prevent the total dehydrogenation to coke, leading to catalyst deactivation[1]. While only a few materials have shown promising results with the traditional thermo-catalytic approach[2], operating conditions remain harsh. The rise of greener catalytic approaches such as plasma technologies offers an alternative path for activating the methane C-H bond under mild conditions while entering the frame of the chemical industry electrification[3]. Cold plasmas provide a rich environment of reactive species able to activate small molecules[4]. However, controlled activation remains challenging, and coke formation is inevitable in traditional configurations. Here, we propose a novel reactor, using two dielectric barriers (in quartz) and circulating water as the ground electrode, effectively preventing carbon deposition with very high selectivity towards alkanes. The effects of power, water temperature, and gap size have been investigated, analyzing energy efficiency, product and hydrocarbon selectivity, and carbon balances.

Results and Discussion

The proposed reactor has first been compared to a traditional DBD reactor made of alumina, and, while the effective plasma power to conversion is almost equal, differences are observed in the gaseous products, as well as in solid deposits. The tubular reactor, using water as the ground electrode, effectively helped to prevent the formation of black carbon by reducing the intensity of the micro-discharges, however, a yellowish film was formed. The effects of varying the water temperature did not significantly alter the performances; however, this parameter could play a fundamental role in preventing the condensation of heavier hydrocarbons, potentially resulting in the development of a polymeric film through a gelling mechanism. The influence of gap modification, through adjustments to the diameter of the internal electrode, was also studied. When the gap was narrowed to the micrometric range (0.5 mm), the plasma chemistry was completely modified resulting in a selectivity near 100% towards alkanes. Furthermore, after a brief plasma modification (wetting) of the quartz reactor wall, the carbon balance was almost equal to 100% and no carbon deposits were observable after the reaction. Moreover, the direct visualization of plasma has allowed an interpretation of its dynamic character. In conclusion, we have demonstrated an alternative plasma technology as an

effective method for non-oxidative methane conversion to hydrocarbons, preventing coke formation, while offering a very high control of product selectivity.

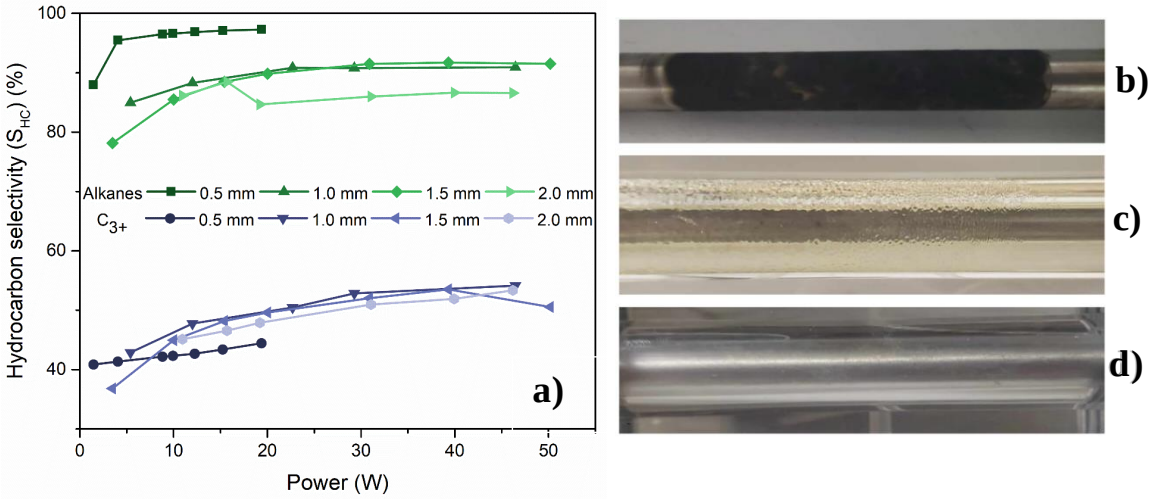


Figure 1. (a) Effect of gap size on hydrocarbon selectivity to alkanes and C_{3+} hydrocarbons with the water-electrode reactor. Reaction conditions: frequency 35kHz, water temperature 50°C, feed flow 50 mL min^{-1} (50% CH_4, bal. Ar), plasma length 10 cm. Optical pictures after reaction of **(b)** inner electrode of traditional DBD reactor with a gap of 1.5 mm **(c)** water electrode reactor with a gap of 1.5mm, and **(d)** water electrode reactor with a 0.5 mm gap.

References

1. P. Schwach, X. Pan, X. Bao, *Chemical reviews* **2017**, *117*, 8497–8520
2. G. Xiaoguang, F. Guangzong, L. Gang, M. Hao, F. Hongjun, Y. Liang, M. Chao, W. Xing, D. Dehui, W. Mingming, *Science (New York, N.Y.)* **2014**, *344*, 616–619.
3. T. Nozaki, K. Okazaki, *Catalysis Today* **2013**, *211*, 29–38.
4. V. Longo, G. Centi, S. Perathoner, C. Genovese, *Current Opinion in Green and Sustainable Chemistry,* **2024,** 46, 100893

Acknowledgements

We acknowledge financial support from the European Research Council under the European Union's Horizon 2020 Research and Innovation Program (grant agreement No 810182 – ERC Synergy project SCOPE *Surface-COnfined fast-modulated Plasma for process and Energy intensification in small molecules conversion*) and the Horizon Europe project (ID: 101115456) "SUPERVAL, *SUstainable PhotoElectRochemical VALorization of flue gases*".

Intrinsic metal-support interactions break the activity-stability dilemma in electrocatalysis

Lingxi Zhou[1], Menghao Yang[2], Yihong Liu[2], Feiyu Kang[3,4] and Ruitao Lv[*1,4]

[1] *State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing, China*

[2] *Shanghai Key Laboratory for R&D and Application of Metallic Functional Materials, School of Materials Science and Engineering, Tongji University, Shanghai, China*

[3] *Institute of Materials Research and Shenzhen Geim Graphene Center, Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen, China*

[4] *Key Laboratory of Advanced Materials (MOE), School of Materials Science and Engineering, Tsinghua University, Beijing, China*

**e-mail corresponding: lvruitao@tsinghua.edu.cn*

Significance and Relevance

We report the very first 'chemical steam deposition (CSD)' strategy armed with machine learning method to synthesize an integrated ruthenium-titanium-manganese ($RuTiMnO_x$) electrode featuring 'intrinsic metal-support interactions' (Figure 1). These interactions induced a self-healing mechanism during the OER for H_2 production, thereby enabling both high activity and stability across the full pH range. The CSD strategy enables 'bottom-up' atomic-scale nanomaterial synthesis, and 'intrinsic metal-support interactions' pave the way to overcome the activity-stability challenge in electrocatalysis.

Preferred and 2nd choice for the topic: H_2 storage and transportation, green H_2 production, hydrogen vectors; Advanced process with electrocatalysis and plasma utilization
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The global energy crisis and climate issues urgently require green energy technologies,[1] with electrocatalysis occupying a pivotal position in clean energy conversion processes essential for future technologies.[2] However, the long-standing dilemma between the activity and the stability of electrocatalysts poses significant constraints on the practical applications, particularly in the case of oxygen evolution reaction (OER) for producing H_2 and other solar fuels.[3]

Here, we report the very first 'chemical steam deposition (CSD)' strategy armed with machine learning method to synthesize an integrated $RuTiMnO_x$ electrode featuring 'intrinsic metal-support interactions' (Figure 1). Employing machine learning, we efficiently identified the optimal atomic metal-support ratio considering both activity and stability metrics, avoiding traditional trial-and-error approaches.

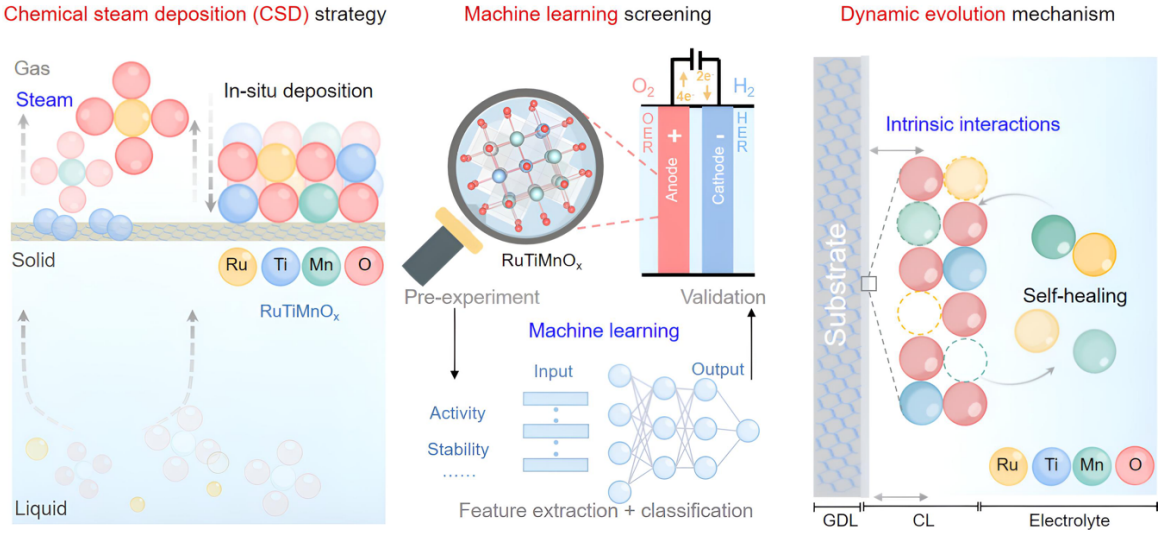


Figure 1. Chemical steam deposition synthesis, machine-learning-assisted screening and catalysis mechanism study of $RuTiMnO_x$.

Results and Discussion

The resulting electrodes achieved high pH-universal mass activities, 48.5, 112.8 and 74.6 times those of benchmark ruthenium oxides in acidic, neutral and alkaline conditions, respectively; and stable operation for up to 3,000 hours in the challenging pH=0 media, a multi-fold improvement in stability over the reported advanced catalysts (Table 1). Extensive in-situ characterizations combined with theoretical calculations have unveiled the pivotal role of intrinsic metal-support interactions and their dynamic evolution mechanisms in breaking the activity-stability dilemma in OER. Our findings open a new avenue of manipulating intrinsic metal-support interactions to overcome the activity-stability tradeoff dilemma in electrocatalysis.

Table 1. Comparison of catalytic performance of different OER catalysts

Media	Sample	η_{10} (mV)	Stable Time (h) @ 10 mA cm^{-2}	Electrolyte	Data source
Acidic	$RuTiMnO_x$	165.2	3000	0.5 M H_2SO_4	This work
	RuO_2	224.1	4	0.5 M H_2SO_4	This work
	$CoWO_4$-delaminated	288	175	0.5 M H_2SO_4	*Science* 384, 1373 (2024)
	LMCF	370	360	0.1 M $HClO_4$	*Science* 380, 609 (2023)
	Ni-RuO_2	214	200	0.1 M $HClO_4$	*Nat. Mater*. 22, 100 (2023)
Neutral	$RuTiMnO_x$	233.5	1500	0.5 M PBS	This work
	RuO_2	335.4	5	0.5 M PBS	This work
	Ru-VO_2	269	60	1.0 M PBS	*Adv. Mater*. 36, 2310690 (2024)
	Ni-$FeWO_4$@WO_3/NF	235	200	1.0 M PBS	*Adv. Mater*. 36, 2308925 (2024)
Alkaline	$RuTiMnO_x$	185.6	2000	1.0 M KOH	This work
	RuO_2	239.6	10	1.0 M KOH	This work
	FeCo−N_3O_3@C	298	240	0.1 M KOH	*Nat. Synth*. 3, 878-890 (2024)
	W-718a	320±10	48 h @ 5 mA cm^{-2}	0.1 M KOH	*Nat. Mater*. 23, 252-261 (2024)

References

1. L. Zhou, Y. Shao, F. Yin, J. Li,* R. Lv,* *Nat. Commun*. **2023**, 14, 7644.
2. L. Zhou, Z. Huang, F. Kang, R. Lv,* *Chem. Eng. J*. **2023**, 458, 141457.
3. L. Zhou, R. Lv* *J. Energy Chem*. **2022**, 70, 310-331.
4. L. Zhou, M. Guo, Y. Li, et al. *Chem. Commun*. **2019**, 55, 4218.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (grant numbers 52371228 (R.L.) and 52302302 (M.Y.)), the National Key Research and Development Program of China (grant number 2021YFA1200013 (R.L.)) and Tsinghua University-Toyota Joint Research Center for Hydrogen Energy and Fuel Cell Technology of Vehicles (grant to R.L.). We thank R. X. Zhou and Y. F. Li for technical support, and Q. M. Yuan and G. S. Liao for experimental assistance.

N_2O decomposition on Fe/CHA catalyst using transient response methods

Maria Elena AZZONI[1], Nicola USBERTI[1], Andrea GJETJA[1], Isabella NOVA[1], Enrico TRONCONI[1]*,
Roberta VILLAMAINA[2], Maria Pia RUGGERI[2], Veselina GEORGIEVA[2], Loredana MANTAROSIE[2], Jill COLLIER[2]
[1]*Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia,*
Politecnico di Milano, Via La Masa, 34, 20156 Milan, Italy
[2]*Johnson Matthey Technology Centre, Blounts Court Road, Sonning Common, Reading RG4 9NH, UK*
** enrico.tronconi@polimi.it*

Significance and Relevance

The decomposition of N_2O, a strong greenhouse gas, has been investigated on Fe/CHA catalysts by Transient Response Methods. A set of transient experiments has been defined to investigate the kinetics of N_2O decomposition. These experiments allowed to gather information on the dynamics and kinetics of the reactions, while the subsequent temperature ramps have given important information on the yet not well understood auto-reduction of Fe. Finally, the oxidation state of Fe after the N_2O decomposition has been assessed by $NO+NH_3$ reduction studies. All the data are then pulled together and considered to model the N_2O decomposition reaction.

Preferred and 2nd choice for the topic: Automotive and stationary emission control (or Fundamental advances in understanding catalysis)
Preferred presentation: Oral only

Introduction and Motivations

Nitrous oxide (N_2O) is a strong pollutant known to have a global-warming impact of almost 300 times higher than carbon dioxide (CO_2)[1]. Among the possible catalysts for the abatement of N_2O, Fe/zeolites represent a valid solution both for their stability, low cost and elevated turnover rates[2,3]. The mechanism for catalytic N_2O decomposition has been extensively studied; however, due to the diverse configuration of the Fe sites involved in the reaction mechanism, the nature and the chemistry of the active species involved remain largely unclear. In this work transient methods are used to investigate iron/chabazite (Fe/CHA) catalysts, promising materials both for NH_3-SCR and N_2O abatement. Eventually, the experimental data are analysed using a PFR transient integral model using a similar approach to that previously used to study redox NH_3-SCR mechanism on Cu/CHA[4].

Materials and Methods

Three different Fe/CHA samples with increasing iron loadings (1% - 2.5% w/w) are investigated in the form of powders (48mg) loaded in a quartz-tube reactor. In all the experiments He is used as a carrier gas and the concentrations of the species are detected through an FT-IR gas analyser and a Mass spectrometer.
N_2O decomposition activity is investigated carrying out Transient Response Methods (TRM) tests: after a pre-reduction with 500 ppm of NO and 500ppm of NH_3, for 1 hour at 550°C, N_2O decomposition is then performed at lower temperatures, either 330, 380 or 430 °C, feeding 500 ppm of N_2O. Then, two different steps are used to investigate the status of the catalyst after the N_2O decomposition: 1) a Temperature Programmed Desorption (TPD) ramp at 15°C/min is run from the decomposition temperature to 550 °C (He carrier, Ar tracer, GHSV= 266250 Ncc/(h*g_{cat})); 2) a reduction step is performed: 500 ppm NO, 500 ppm NH_3 are fed isothermally (330 °C) for 1 h 20 min (He carrier, Ar tracer, GHSV= 266250 Ncc/(h*g_{cat})). Lastly, the integral consumption of NO (µmol) and integral of the production of N_2 (µmol) are calculated.

Results and Discussion

On all the samples, a significant consumption of N_2O is observed right after its feed, leading to the simultaneous mirror-like production of N_2 followed, after a few seconds, by the production of O_2 (as

shown in Figure 1, panel A). For all the Fe/CHA catalysts, the stoichiometric ratio between N_2O consumed and N_2 and O_2 produced follows the expected of 2:2:1 stoichiometry of the N_2O decomposition ($2N_2O \rightarrow 2N_2 + O_2$) after the initial dynamics. It is worth noticing that N_2O is not adsorbed on the catalyst since there is no release during the final temperature ramp (Figure 1, panel B). However, an evolution of stored oxygen in TPD is present on all the sample, characterized by a distinct peak in the 380-450°C range. It is associated to the auto-reduction of the Fe, previously oxidized during N_2O feed step. When NO+NH_3 reduction protocol is performed after the N_2O decomposition step, consumption of NO and production of N_2 are observed. This is due to the ability of N_2O to re-oxidize the iron sites while decomposing. Calculating the $NO_{consumed}/Fe_{sample}$ ratio for the experiment at the different temperatures it is observed that, as the temperature increases, the ratio decreases evidencing a lower consumption of NO at the higher temperatures (e.g., for the intermediate sample, from 330 to 430 °C the ratio reduces from 67 to 58 %).

This behaviour can also be explained with the ability of Fe sites to "auto reduce" at higher temperatures, thus, less Fe can participate in the following NO + NH_3 reduction. This auto-reduction confirms why when N_2O is fed at these higher temperatures is strongly consumed.

As a preliminary analysis, a Transient Kinetic Analysis (TKA) is performed on the experimental data by means of a PFR transient integral model which incorporates the N_2O decomposition chemistry as a redox mechanism. The redox model for low-T NH_3-SCR over Cu/CHA involved only one active Cu species[4]. Contrarily, for N_2O decomposition on Fe/CHA, this single-site approach fails to model the dynamic profile with accuracy, suggesting the involvement of more than one Fe active site. An example of multi-site model fit is shown in the left panel of Figure 1 as transparent lines.

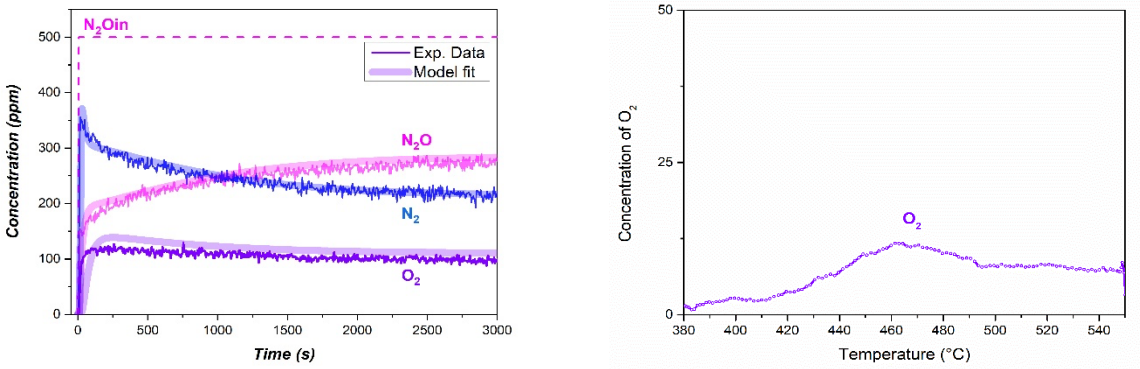


Figure 1 Evolution of N_2, N_2O and O_2 during the feed of 500ppm of N_2O for 1 hour on a Fe/CHA sample pre-reduced (left) and successive evolution of O_2 during Temperature Programmed Desorption (right)

References

1. M. Koebel, M. Elsener, T. Marti, *Combustion Science and Technology*, **1996**, *121*, 85–102.
2. F. Gao, Y. Wang, M. Kollár, N. M. Washton, J. Szanyi, C. H. F. Peden, *Catalysis Today*, **2015,** *258*, 347–358.
3. A. Wang, Y. Wang, E. D. Walter, R. K. Kukkadapu, Y. Guo, G. Lu, R. S. Weber, Y. Wang, C. H. F. Peden, F. Gao, *Journal of Catalysis*, **2018**, *358*, 199–210.
4. N. D. Nasello, U. Iacobone, N. Usberti, A. Gjetja, I. Nova, E. Tronconi, R. Villamaina, M. P. Ruggeri, D. Bounechada, A. P. E. York, J. Collier, *ACS Catalysis* **2024**, *14, 6*, 4265-4276.

Acknowledgements

This work was financially supported by Johnson Matthey.

Pilot-Scale Evaluation of a Multi-Promoters Modified V/Ti-Based SCR Catalyst for Medium-Low Temperature DeNOx in Coking Plant Flue Gas

LI-YI CHEN*, CHI-LANG CHEN, WEN-CHANG CHEN

[1]*New Materials Research & Development Department, China Steel Corporation, No. 1, Zhonggang Rd., Xiaogang Dist., Kaohsiung City, Taiwan*

** 189621@mail.csc.com.tw*

Significance and Relevance

We developed a novel multi-promoters modified V/Ti-based (MPV) SCR catalyst for effective denitrification (DeNOx) at medium-low temperatures (220–250°C), demonstrating good sulfur resistance. Plate-type MPV SCR catalysts were fabricated and tested for NH_3-SCR activity within the medium-low temperature range for coke oven flue gas. Results of pilot test showed that at 215°C, NO_x reduction exceeded 99%, with stable performance over a 72-hour test. This study confirms the catalyst's effectiveness and its potential for energy savings and carbon reduction in coke oven gas treatment applications.

Preferred and 2nd choice for the topic: *Automotive and stationary emission control or Air cleaning and combustion*

Preferred presentation**:** Oral preferred or Short Oral

Introduction and Motivations

The coke oven process is essential in ironmaking, providing both fuel and a reducing agent for the blast furnace. NH_3-SCR technology is widely used to control NO_x emissions from coke oven flue gas[1,2]. Recently, there has been a shift from high-temperature (300–400°C) to medium-low temperature (200–250°C) NH_3-SCR technology to save heating energy. In this study, we developed a multi-promoters modified V/Ti-based (MPV) SCR catalyst with good sulfur resistance. Pilot-scale testing was conducted on plate-type MPV SCR catalysts for coke oven flue gas, examining how variations in operating conditions, temperature, and flow rate impact DeNOx efficiency. These findings provide valuable technical insights for coke oven flue gas denitrification, with potential to drive progress in the field.

Results and Discussion

1. Catalyst activity and SO_2 resistance of the MPV SCR catalyst

A MPV SCR catalyst was synthesized by impregnating the active vanadium with three kinds of promoters onto an anatase (TiO_2) support, followed by calcination at 500°C for 4 hours. We further tested the DeNOx activity of the MPV SCR catalyst under simulated flue gas at various reaction temperatures. As shown in **Figure 1(a)**, the DeNOx efficiency of the catalyst was >90 % at 220–250°C. In the **Figure 1(b)**, we observed the long-term effects of high H_2O and high SO_2 environments on the DeNOx efficiency of the MPV SCR catalyst. The DeNOx efficiency of the catalyst decreased from 99.5% to 80% as exposure time to high H_2O and high SO_2 conditions is extended from 1 hour to 32 hours.

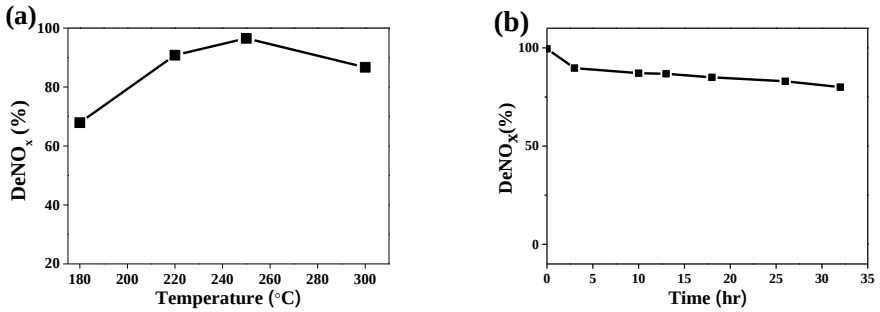


Figure 1. The activity tests of the granule-type MPV SCR catalyst in simulated flue gas; (a) effect of temperature on the $DeNO_x$ efficiency of the catalyst at 200 ppm NO, 3% O_2, NH_3/NO=1, GHSV: 27,751 h^{-1}. (b) long-term effects on the $DeNO_x$ efficiency of the catalyst at 200 ppm NO, 3% O_2, NH_3/NO=1, 14%H_2O, 1000 ppm SO_2, and GHSV of 27,751 h^{-1}.

2. Pilot-scale test and the evaluation of MPV SCR catalyst activity

A self-designed SCR pilot plant has been constructed and tested at CSC (China Steel Corporation). It is set up beside the #1 coke oven plant as shown in **Figure 2(a)**, which has dimensions of 2.3 × 2.2 × 3.05 m and was designed to a maximum gas flow of 240 m^3/h. The schematic diagram in **Figure 2(b)** illustrates the pilot-scale equipment composed of a heater, a catalyst bed, and a draught fan. A total of four plate-type SCR catalyst modules were filled in the catalyst bed, each measuring 15×15×15 cm and with a total volume of 0.0135 m^3. The SCR reaction utilized 10% ammonia-water solution as a reducing agent, which was mixed with the flue gas upstream. A portable flue gas analyzer (PG-300, Horiba, Japan) was used to analyze the composition of the flue gas both before and after the SCR reactor.

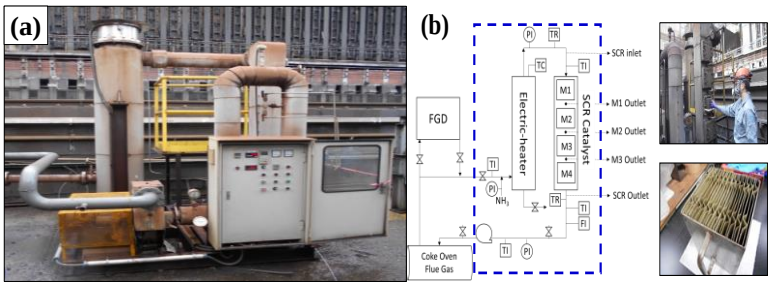


Figure 2. (a) Picture of the self-designed SCR pilot plant；(b) schematic diagram of pilot-scale test for the plate-type MPV SCR catalyst；dashed square referred to the SCR pilot.

As shown in Figure 3(a), the optimal temperature for the MPV SCR catalyst is between 210–268°C in pilot-scale test, achieving DeNOx efficiencies of over 95%, consistent with the laboratory-simulated flue gas DeNOx test results. Table 1 shows that under varying flue gas conditions (Coke Oven Gas: COG, Mixed Gas: MG) and operation periods (up to 72 hours), the MPV SCR catalyst achieved a DeNOx efficiency of over 97.5% at operating temperatures between 190–215°C.

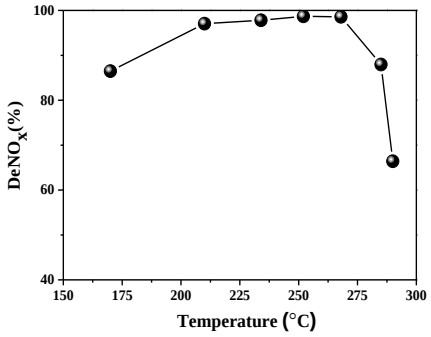


Figure 3. Effect of temperature on the DeNOx efficiency at the outlet of the MPV SCR catalyst module with a GHSV of 3,185-3,500 h^{-1}.

Table 1. The DeNOx efficiency at the outlet of SCR pilot reactor under different coke oven flue gas conditions.

Gas Type	Operation Time (hr)	GHSV (hr^{-1})	Temp (°C)	$DeNO_x$(%)
COG	1	4,500	207	97.5
MG	1	3000	190	99.8
MG	72	4,500	215	99.2

Here, we successfully fabricated plate-type MPV SCR catalysts and tested their NH_3-SCR catalytic activity in the medium-low temperature range of coke oven flue gas. The results showed that at an operating temperature of 215°C, the NO_x reduction exceeded 99%, maintaining stability over a 72-hour operating period. This study not only demonstrated the effectiveness of the catalyst, but also its successful application of medium-low temperature DeNOx catalyst technology for treating coke oven gas, with significant potential for energy savings and carbon reduction benefits.

References

1. P. Cavaliere, *Springer, cham.* **2019**, 39-110.
2. J. Yu, C. Li, F. Guo, S. Gao, Z.G. Zhang, K. Matsuoka, G. Xu, *Fuel*. **2018**, 37-49.

Acknowledgements

We are grateful for the support from the China Steel Company and supervisors and especially thank T6S, T75, and W21 for the pilot establishment and NO measurement.

New Technologies for Sustainable Valorisation of CH_4 and CO_2 from Livestock and Biogas

Ilenia ROSSETTI[1,2,*], Alice GRAMEGNA[1,2], Matteo TOMMASI[1], Simge Naz DEGERLI[2], Gianguido RAMIS[3]
[1] *Chemical Plants and Industrial Chemistry Group, Dip. Chimica, Università degli Studi di Milano, Via C. Golgi 19, 20133 Milan, Italy*
[2] *INSTM Unit Milano-Università, Via C. Golgi 19, 20133 Milan, Italy*
[3] *DICCA, Università degli Studi Genova, via all'Opera Pia 15A, 16145 Genoa, Italy*
** e-mail ilenia.rossetti@unimi.it*

Significance and Relevance

Different adsorbents were tested in silico, then the selected ones in a controlled microreactor and in a real stable to design an adsorption-based process for the direct air capture of CO_2 and CH_4. A pilot scale (currently under realisation) and a full scale plant were designed from these data. This plant has a better capacity and utilisation if coupled with biogas upgrade to biomethane. The valorisation of CO_2 from biogas is integrated in the process by demonstrating the feasibility of a methanation reactor.

Preferred and 2nd choice for the topic: 1) CO2 utilisation and recycling; 2) Air cleaning and combustion
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Ruminants, mainly dairy cattle, are widely recognized as one of the main contributors to methane emissions in the environment, playing a significant role in the global warming phenomenon. Considering that a cow emits about 500 L/d of methane and in view of the increasing population of cows due to the intensive farming activities, the daily methane emission is considerable. It is estimated that a cattle (600 kg of body weight) consumes 21 kg DMI /day and due to the enteric fermentation and respiration releases 23 g CH_4 / kg DMI and 647 g CO_2 / kg DMI. Extensive efforts have been made to reduce methane emissions from ruminants prior to their release into the environment; however, considering that the enteric fermentation process is unavoidable, it is crucial to establish methods for capturing the emitted methane.

Given the common practice of implementing forced ventilation within barns for animal well-being, the discussed process aims to capture methane via adsorption on either synthetic or natural zeolites or different active carbons through the barn ventilation. Great limitations come from the Direct Air Capture of both gases due to their limited partical pressure and therefore low adsorption equilibrium concentrations.

The same two greenhouse gases coexist in the same productive frame as product of the anaerobic digestion of waste agro-zootechnical wastes. Therefore, the same adsorption system can be implemented efficiently also for the upgrade of biogas to biomethane, acting as a CO_2 capture technology. After saturation with the barn adsorption. The subsequent valorisation of the captured CO_2 to synthetic methane through the Sabatier reaction is then considered. These three integrated strategies offer the possibility to improve the sustainability of the zootechnical sector.

In this work, both experimental and process simulation methods have been coupled for the design of pilot scale plants and the relative scaled up design to full scale. Different options to improve the sustainability of intensive farming and biogas production and upgrade to biomethane have been designed and compared.

Materials and Methods

The adsorption isotherms of the gases on the selected adsorbent materials were first taken from the literature and then validated through experiments using a Hiden Catlab apparatus. Both saturation isotherms and dynamic breakthrough curves have been collected. Process design has been performed using Aspen Adsorption® V11 software after retrieving the relevant kinetic, transport and thermodynamic parameters. Different adsorbents have been exposed into a stable for 3-6-9 weeks in

different locations and then characterized by thermogravimetry and by temperature programmed desorption coupled with mass spectrometry.

Ni-based catalysts (5-20 wt%) supported over CeO_2, SiO_2, Al_2O_3 and ZrO_2 have been prepared by impregnation and co-precipitation. Testing has been done under practically relevant conditions at pressure up to 20 bar, with a stoichiometric H_2/CO_2 feed, considering the Sabatier reaction for the methanation of CO_2. Process design has been accomplished with Aspen Plus process simulator.

Results and Discussion

Carbon dioxide poses a significant challenge for methane capture on zeolites, because adsorption competition exists between CO_2 and CH_4. The adsorption process is dominated by the carbon dioxide adsorption. This revealed the necessity of a two-stage adsorption system, with two beds in series. An initial “guard bed” filled with zeolite 13X was used to adsorb carbon dioxide and other gases from the barn, while efficiently adsorbing methane in the second bed of the same volume filled with Clinoptilolite, a cost-effective natural zeolite with excellent properties for methane adsorption. With the current design configuration, the first bed reaches saturation in 210 days whereas the second bed reaches saturation in 40 days; consequently, five replacements need to be executed while keeping the guard bed in operation. The designed plant allows to obtain an exiting flow consisting only of air, therefore mitigating the environmental impact of the agricultural sector.

As for CO_2 utilisation, we considered a biogas production facility. H_2 is considered as produced from water electrolysis fed with renewable power. A key issue is the strong exothermicity of the reaction. Our research explores the use of water vapour, added on purpose to the reactor as a thermal vector and later condensed. The simplest and most economical reactor arrangement is composed of a certain number of adiabatic catalytic beds (up to five) with intercooling. Alternative arrangement has been explored designing a fluidized-bed reactor, that allows better temperature control, but this led to incomplete conversion and it was difficult to scale-up.

The possibility to use the methane already present in biogas as diluent (i.e. thermal vector to control the exothermicity) was also considered, offering the additional advantage to eliminate the otherwise needed and expensive CO_2 capture step.

This option is intended to improve the CH_4 yield and to meet the purity specifications for feeding the natural gas distribution grid. Possible poisons for the methanation catalyst, such as sulphides or nitrogen containing poisons, were considered and removed by the adsorption pretreatment. Two options were further considered, one with preliminary CO_2 separation from biogas and methanation of pure carbon dioxide, the other one with direct treatment of the biogas stream.

At least 4 reactive stages for the methanation reaction were needed to get > 75% conversion. Either adiabatic or cooled catalytic beds were compared, operating below 400°C.

Acknowledgements

This study was carried out within the Agritech National Research Center and received funding from the European Union Next-Generation EU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) – MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.4 – D.D. 1032 17/06/2022, CN00000022).

Modeling of Cu/SSZ-13 SCR catalyst sulfation depending on HTA-induced changes in ZCuOH and Z_2Cu site distribution

Tetyana ZHELEZNYAK[1], Petr KOČÍ[*,1], William S. EPLING[2]
[1]*University of Chemistry and Technology, Dept. of Chemical Engineering, Technická 5, Prague, Czech Republic.*
[2] *University of Virginia, Dept. of Chemical Engineering, 385 McCormick Rd, Charlottesville, USA.*
**petr.koci@vscht.cz*

Significance and Relevance

Selective catalytic reduction (SCR) of nitrogen oxides (NOx) remains a key topic in environmental catalysis, and catalyst aging and sulfur poisoning are critical issues for practical application. The novel aspect of this work lies in developing a mathematical model that captures changes of ZCuOH and Z_2Cu site distribution during hydrothermal aging of Cu/SSZ-13 SCR catalyst and combines them with the SO_2 oxidation and sulfation kinetics specific to the individual Cu site types. The model offers a deeper understanding of the degradation mechanisms, which is crucial for predicting catalyst lifespan and optimizing SCR technology for reliable NO_x emissions control in real-world conditions.

Preferred and 2nd choice for the topic: Automotive and stationary emission control, Air cleaning and combustion
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Selective catalytic reduction (SCR) with Cu/SSZ-13 catalysts is the leading approach for reducing nitrogen oxides (NOx) emissions from diesel engines. Within the catalyst, various active sites exist, including mono- and multinuclear framework copper sites and extra-framework CuO nanoparticles[1]. The literature primarily discusses two framework sites: ZCuOH and Z_2Cu. The main mechanisms of Cu/SSZ-13 catalyst deactivation are hydrothermal aging (HTA) and sulfur poisoning. Mild HTA, at temperatures below 750°C, preserves the zeolite structure but promotes the transformation of ZCuOH sites to Z_2Cu, affecting catalyst performance[2]. Recently we developed a kinetic model that describes transformation of the Cu sites during mild HTA and quantified different activity of ZCuOH and Z_2Cu sites in NO, CO, NH_3 and SO_2 oxidation reactions[3]. This work utilizes an integrated experimental and kinetic modeling approach to examine the effect of combined HTA and sulfur poisoning on the standard SCR reaction rate.

Materials and Methods

The Cu/SSZ-13 catalyst used in this study was provided by Cummins Inc. and was washcoated onto a cordierite monolith structure with a cell density of 600 cpsi. The SSZ-13 zeolite had a Si:Al ratio of 9.5, and the copper loading was 2.2 wt.%. All experiments were performed in a tubular flow lab reactor. In situ techniques, including diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), NH_3-TPD, H_2-TPR, and NH_3+NO titration, were utilized to quantify the active sites in the catalyst samples. The SCR reaction was investigated at steady-state over a temperature range of 150–500 °C, comparing the activity of the catalyst in four different states: (i) fresh catalyst, (ii) fresh catalyst sulfated at 400°C, (iii) hydrothermally aged catalyst, and (iv) hydrothermally aged catalyst sulfated at 400°C. Mild hydrothermal aging was performed at 650 °C for 5 hours. Both fresh and hydrothermally aged samples were sulfated in the presence of 30 ppm SO_2, 10% O_2, 7% H_2O, and balance N_2 at 400 °C. A heterogeneous 1D plug-flow model was used to simulate transport and reactions in the catalyst, incorporating mass and enthalpy balances for the gas and solid phases along the reactor. The kinetic

equations include NH_3 adsorption/desorption, SCR reaction, NH_3 oxidation, SO_2 oxidation, and sulfur deposition on Cu sites.

Results and Discussion

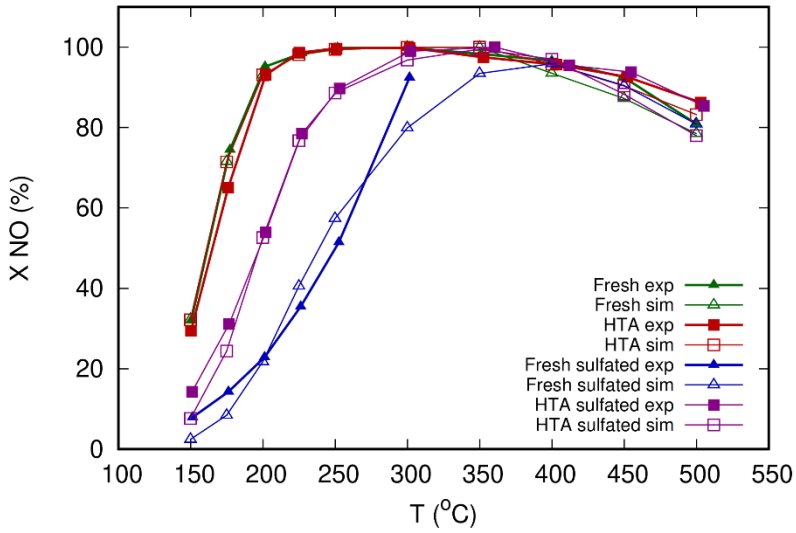


Figure 1. NOx conversion under standard SCR reaction conditions on fresh and hydrothermally aged (HTA) catalysts before and after SO_2 exposure. Full points – experiments, hollow points – simulation results.

First, a kinetic model that describes the changes in ZCuOH and Z_2Cu site concentrations during hydrothermal aging was developed using the information from catalyst characterization. The model can predict the rate of Cu site transformation depending on temperature and actual site concentrations[3]. Subsequently, a simulation study was conducted to describe the impact of sulfur poisoning on the fresh and hydrothermally aged samples' performance during standard the SCR reaction, Figure 1. The fresh and HTA samples show practically identical NO_x conversions as the dominant process in HTA is just a transformation from ZCuOH to Z_2Cu, and both sites exhibit similar SCR activity.

However, much larger differences exist after exposure to sulfur. The impact of sulfur poisoning is more pronounced on the fresh catalyst, leaving effectively only 4% of the Cu site activity compared to the fresh state. The hydrothermally aged is not affected as much, retaining 14% of the original activity. This trend is attributed to the transformation of ZCuOH sites to Z_2Cu sites during hydrothermal aging and the fact that Z_2Cu sites are less susceptible to sulfur poisoning than ZCuOH. This trend is further promoted by the higher activity of ZCuOH sites for SO_2 oxidation to SO_3 that binds more strongly to the catalyst surface.

The developed reaction kinetic model provides rational background for the observed phenomena and allows prediction of the catalyst performance in sulfur-containing environment depending on the actual distribution of ZCuOH and Z_2Cu sites in the catalyst as it may change during the catalyst lifetime.

References

1. C. Paolucci, A. A. Parekh, I. Khurana, J. R. Di Iorio, H. Li, J. D. Albarracin Caballero, A. J. Shih, T. Anggara, W. N. Delgass, J. T. Miller, F. H Ribeiro, R. Gounder, W. F. Schneider, *J. Am. Chem. Soc.* **2016**, *138 (18)*, 6028-6048.
2. L. Wei, Y.-R. Chen, S. Marino, Y. Gu, W. S. Epling, *Chem. Eng. J.* **2023**, *467*, 143318.
3. T. Zheleznyak, P. Kočí, W. S. Epling, *Chem. Eng. J.* **2024**, *489*, 151194.

Porous Materials and CO_2 capture

Silvia BRACCO[1], Jacopo PEREGO[1], Charl X. BEZUIDENHOUT[1], Armando RIGAMONTI[1,2], Angiolina COMOTTI[*,1]
[1]*University of Milano-Bicocca, Dept. of Materials Science, Via R. Cozzi 55, Milan, Italy.*
[2] *University of Messina, Dept. of Chem., Biol., Pharm. and Environ. Sciences, Via F. Stagno d'Alcontres 31, Messina, Italy.*
** e-mail angiolina.comotti@unimib.it*

Significance and Relevance

The increase in CO_2 emissions has stimulated scientific and technological developments to capture, convert, store, and remove CO_2 from the environment. We propose porous materials able to capture and separate CO_2 from N_2 by exploiting the active sites of the framework, which can host specifically CO_2 molecules. The intermolecular interactions of about 35 kJ/mol are a very good balance for favorable CO_2 capture and release. Breakthrough experiments demonstrate the efficient CO_2 separation starting from CO_2/N_2 mixtures at room temperature.

Introduction and Motivations

CO_2 capture from industry or directly from the atmosphere is a topic of extreme importance on a global scale because of the drastic climate changes, threating our ecosystem.[1] CO_2 capture technology relied on liquid amine scrubbing but due to its high energy consumption and corrosive property, CO_2 capture using solid materials has recently come a valid alternative way. The manufacture of porous materials is one of the major challenges and their permanent and tunable porosity brought them into the active research area of carbon capture and utilization (CCU) by physisorption processes which require low energy costs for gas uptake and release. This goal can be achieved through various strategies that promote the formation of metal–organic frameworks (MOFs) and porous organic frameworks or polymers (POFs or POPs).[2,3] They are diversified by their tendency to form stable structures and their degree of crystalline periodicity.

MOFs are constructed by the self-assembly of organic ligands coordinated to metal ions or metal clusters generating structures with permanent porosity, high specific surface areas and tunable topologies. Within the family of MOFs the presence of a second linker enabled to further tailor the structures generating the so-called pillar-layered MOFs. Pillars in MOFs are composed by two distinct organic ligands, one ligand is coordinated to metal nodes forming two-dimensional sheets, whilst the other one, called pillar, coordinates with the metal ions of two different planes, creating a layered and flexible structure that is suitable for CO_2 capture.

POFs boast some prerogatives derived from the stability of their 3D network of covalent bonds. These prerogatives include high thermal robustness, resistance to solvents, especially water, and remarkable volumetric and gravimetric pore capacities. Further important properties are enabled by the post-synthetic insertion of organic functional groups, each promoting specific interactions with target gas.

Results and Discussion

We fabricated a new class of POFs based on calixarene-moieties which showed outstanding adsorption properties towards CO_2, while selectively excluding N_2.[4] Such architectures enabled to incorporate macrocycle cone-like moieties with preorganized cavities and form functional porous materials containing two hierarchical levels of porosity, due to both the macrocycle shape and the framework pore architecture. These smart architectures endowed with hierarchical porosity from micro- to meso-porosity showed notable sponge-like swellability by CO_2, which was captured effectively at room temperature, even in competition with N_2, yielding CO_2 removal in column breakthrough experiments (Figure 1). POFs offer the opportunity to incorporate photoswitchable molecules into solid-state materials promising for the fabrication of responsive materials, the properties of which can be controlled on-demand.[5] A responsive porous switchable framework was

synthesized by incorporating a bistable chiroptical overcrowded alkene moiety into the backbone of a rigid aromatic framework. As a consequence of the high intrinsic porosity, the resulting framework readily responds to a light stimulus, as demonstrated by solid-state Raman and reflectance spectroscopies. Solid-state ^{13}C NMR spectroscopy highlighted an efficient and quantitative bulk photoisomerization of the incorporated light-responsive overcrowded olefins in the solid material. Taking advantage of the quantitative photoisomerization, the porosity of the framework and the consequent CO_2 adsorption/desorption could be reversibly modulated in response to light and heat.

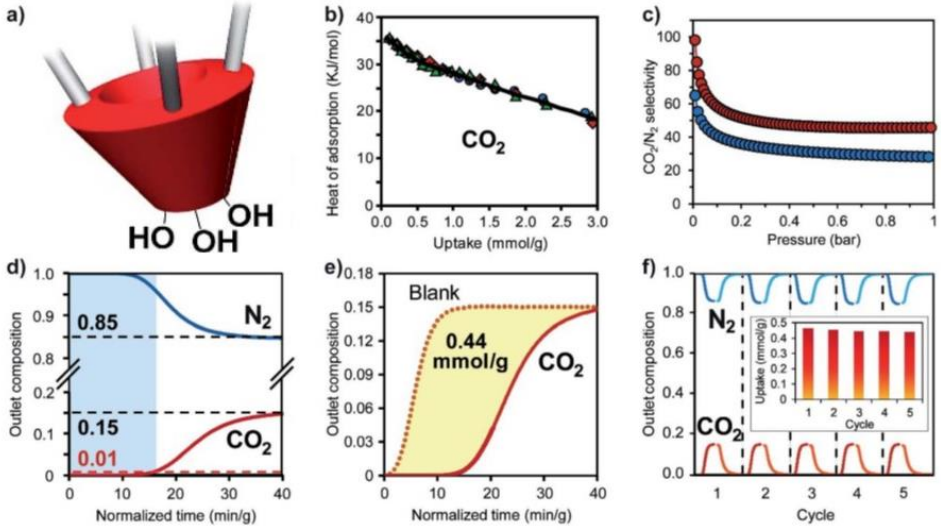


Figure 1 (a) Schematic representation of a calixarene-based POP. (b) Heat of adsorption from a microcalorimeter coupled with adsorption apparatus. (c) CO_2 over N_2 selectivity at 273 K calculated applying IAST theory to a 15 : 85 CO_2/ N_2 mixture. (d) CO_2/N_2 (15/85) breakthrough curves measured with a total flow rate of 4 sccm. (e) CO_2 breakthrough curves: the yellow shaded area was integrated to calculate the total amount of CO_2 adsorbed under dynamic conditions (f) Breakthrough experiments repeated for five cycles. The desorption was carried out by N_2 flow at room temperature. Column efficiency is constant over all cycles.

We propose a category of pillared MOFs consisting of two-dimensional layers of Me^{2+} ions coordinated with the heterocyclic anions and pillars composed of molecules bearing two carboxylate groups as new porous materials for CO_2 capture. The porous materials were characterized by a combined approach that include powder X-ray diffraction for the study of crystalline materials, FT-IR spectroscopy for the identification of functional groups, solid state NMR spectroscopy for the determination of purity and degree of crystallinity of the samples, scanning electron microscopy for the study of morphology. In situ X-ray diffraction experiments using synchrotron source light on the porous material as well as at varying CO_2 pressures, enabled to evaluate structural changes throughout the adsorption process. The MOFs exhibited high selectivity towards CO_2 with respect to N_2 (> 100) even at room temperature, and thus are promising materials for CO_2 capture from flue gas. Notably, such materials can be directly integrated into an electrocatalytic device for the conversion of CO_2 into e-fuels by using renewable energy and water.

References

1. M. S. B. Reddy et al. *RSC Adv*. **2021**, *11*, 12658.
2. M. Ding, R. W. Flaig, H.-L. Jiang, O. M. Yaghi *Chem. Soc. Rev.* **2019**, *48*, 2783.
3. S. Das, P. Heasman, T. Ben, S. Qiu Chem. Rev. 2017, 117, 1515.
4. A. Pedrini, J. Perego, C. X. Bezuidenhout, S. Bracco, P. Sozzani, A. Comotti *J. Mater. Chem A* **2021**, *9*, 27353.
5. F. Castiglioni, W. Danowski, J. Perego, F. K.-C. Leung , P. Sozzani, S. Bracco, S. J. Wezenberg, A. Comotti and B. L. Feringa *Nature Chem.* **2020**, *12*, 595.

Acknowledgements

The authors would like to thank INSTM-DANTE and MUSA-PNRR projects for financial support.

N_2O decomposition using an electric-field-assisted catalysis at low temperatures

Takuma HIGO[1], Ayaka SHIGEMITO[1], Yuki INODA[1], Chihiro UKAI, Kenta MITARAI[2], Yasushi SEKINE[*,1]
[1]*Waseda University, Department of Applied Chemistry, Shinjuku, Tokyo, Japan.*
[2] *Yanmar Holdings, Research & Development Centre, Maibara, Shiga, Japan.*
** ysekine@waseda.jp*

Significance and Relevance

We applied a novel catalytic system, an electric field assisted catalytic system, to nitrous oxide (N_2O) removal, demonstrating that N_2O decomposed into N_2 and O_2 efficiently on the electric field applied Rh catalyst, even at low temperatures below 473 K and in the presence of excess oxygen and water vapour. The reaction mechanism on the catalyst applied with the electric field was investigated using kinetics and various characterisations, which revealed that surface oxygen on the catalyst contributes to N_2O decomposition.

Preferred and 2nd choice for the topic: Air cleaning and combustion and *Automotive and stationary emission control*
Preferred presentation: *Oral preferred or Short Oral*

Introduction and Motivations

N_2O is a greenhouse gas that is about 310 times more effective than CO_2 and is also ozone-depleting, so the development of efficient technologies to mitigate its emissions from various sectors, including agriculture, industry, and transportation. N_2O decomposition using heterogeneous catalysts is one of the most promising methods[1], but it is not yet very versatile because it requires high reaction temperatures. Therefore, we focused on a novel catalytic system, an electric-field-assisted catalytic system, and aimed to achieve N_2O decomposition at lower temperatures[2].

Materials and Methods

We prepared ceria-zirconia ($Ce_{0.7}Zr_{0.3}O_2$) for the catalyst support. Preparation was conducted using a citric acid complex method with aqueous solutions of $Ce(NO_3)_3{\cdot}6H_2O$ and $ZrO(NO_3)_2{\cdot}2H_2O$, with excess amounts of citric acid and ethylene glycol. The molar ratio of metal: citric acid: ethylene glycol was 1: 3: 3. After the obtained solution was dried on a hot plate with stirring. The obtained powder was calcined in air at 1123 K for 10 h. Rh species were loaded on $Ce_{0.7}Zr_{0.3}O_2$ using an impregnation method. A slurry was made by adding a powdered $Ce_{0.7}Zr_{0.3}O_2$ to a solution of $Rh(NO_3)_2$. Then, it was dried at 393 K for 20 h and was calcined in air at 823 K for 3 h.

Catalytic activity tests were conducted in a fixed flow-type quartz reactor at atmospheric pressure. An electric field (EF) was applied using a power supply *via* stainless steel electrodes, contacting the catalyst-bed on the upper and lower sides. A direct current of 6 mA was applied to the catalyst-bed. During this activity test applying the EF, the catalyst-bed temperature was measured directly with a thermocouple to verify the effects on the catalytic activity of Joule heating by the applied direct current. Response voltage was measured using a digital phosphor oscilloscope (TDS 2001C with a voltage probe P6015A; Tektronix Inc.). 100 or 200 mg of catalyst (sieve to 250–500 µm mesh) was placed in a quartz tube. Reactant gases were a mixture comprising 1000 ppm of N_2O, 10%O_2, and 10%H_2O. The total gas flow rate was 100 mL min^{-1}. Also, a thermocouple was set at the bottom of the catalyst bed to measure the actual catalyst bed temperature. The outlet gases were detected using a quadrupole mass spectrometer (Thermostar GSD 350; Pfeiffer Vacuum GmbH).

Results and Discussion

We applied a non-conventional catalytic system, catalytic reactions in an EF, to N_2O decomposition on the 0.5wt%Rh/$Ce_{0.7}Zr_{0.3}O_2$ (Rh/CZO) under 1000 ppm N_2O + 10%O_2 + 10%H_2O. Figure 1 shows the excellent promotion of catalytic activity by application of the electric field, even at low temperatures. To confirm the electronic state of Rh species on CZO both with and without the application of the EF

during N_2O decomposition, operando-XAFS measurements were conducted. As a result, the Rh species was found to be Rh_2O_3, indicating that the N_2O decomposition proceeded on Rh_2O_3 surface with or without the EF.

To gain insight into the promotive effect due to the application of the EF on the catalytic activity, we investigated the dependence of the N_2O conversion rate on the partial pressures of N_2O and O_2. Tests were conducted at 423 K with EF and at 638 K without the EF. The dependence on N_2O partial pressure was slightly reduced by the EF; the reaction order was 0.70 (with EF) and 1.10 (without EF), respectively. On the other hand, the dependence on O_2 partial pressure showed a drastic change by the EF application (Figure 2a). On the catalyst without the EF, the N_2O decomposition was hindered by the coexistence of oxygen; −0.51 of reaction order. In contrast, with the electric field, the reaction order was almost zero (−0.06), indicating that N_2O decomposition is not inhibited by coexisting O_2.

Figure 2b-c presents the N_2/O_2 molar ratio in outlet gas during N_2O decomposition under a flow of 1000 ppm N_2O + 10%H_2O with and without the EF. Figure 2b is the result of the catalyst without the EF, revealing that the N_2/O_2 molar ratio exceeded 2 upon the supply of N_2O, with subsequent saturation to a stoichiometric value of 2. This result suggests that N_2O decomposition proceeds through the Langmuir–Hinshelwood (LH) mechanism; the associative desorption of residual oxygen species is slower than the N–O bond cleavage. By contrast, with the electric field, for 20 min after the reaction started, the N_2/O_2 ratio was below 2. This phenomenon demonstrates that N_2O reacts with oxygen species on the surface of Rh/CZO as follows equation:

$$N_2O\ (g) + O^*(\text{surface}) \rightarrow N_2(g) + O_2(g) + *(\text{surface})$$

In conclusion, it was revealed that surface oxygen contributes actively to N_2O decomposition thanks to the application of EF, leading to significant catalytic activity at low temperatures.

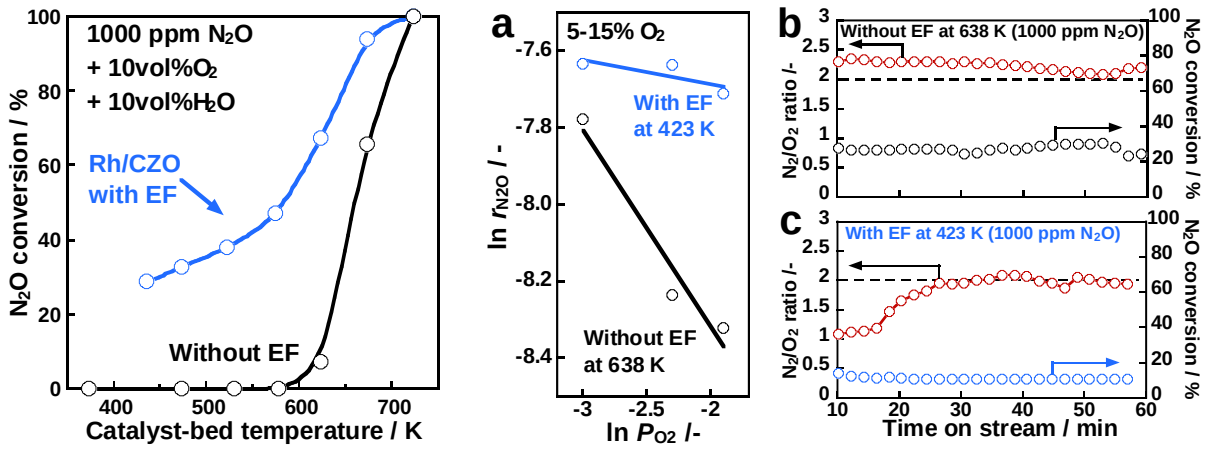


Figure 1. (left) Catalytic activity for N_2O decomposition over 0.5wt%Rh/ $Ce_{0.7}Zr_{0.3}O_2$ with and without the electric field.

Figure 2. (right) (a) Dependence of the decomposition rate of N_2O on the pressure of O_2 and (b) N_2/O_2 molar ratio in out-let gas over 0.5wt%Rh/$Ce_{0.7}Zr_{0.3}O_2$ with and (c) without the electric field.

References

1. M. Konsolakis, *ACS Catal.* **2015**, 5, 6397–6421.
2. A. Shigemoto, T. Higo, C. Ukai, Y. Inoda, K. Mitarai, Y. Sekine, *Catal. Sci. Technol*. 2024, 14, 4471-4478.

Acknowledgements

The authors thank Prof. Seiji Yamazoe (Tokyo Metropolitan University) for great assistance in the XAFS analysis. A part of this work was supported by JSPS KAKENHI (grant no. 22K20484, 23H05404 and 23K20034) from the Japan Society for the Promotion of Science.

Effect of promoters on the performance of Pt/TiO_2 catalyst for NO_x removal by selective catalytic reduction (SCR) with H_2

Marc Maurer[1], Maria Casapu[2], Jan-Dierk Grunwaldt[1,2]
[1]*Karlsruhe Institute of Technology (KIT), Institute of Catalysis Research and Technology (IKFT), Hermann-von-Helmholtz-Platz 1, Karlsruhe, Germany.*
[2] *Karlsruhe Institute of Technology (KIT), Institute for Chemical Technology and Polymer Chemistry (ITCP), Engesserstraße 20, Karlsruhe, Germany.*
**grunwaldt@kit.edu*

Significance and Relevance

The influence of basic (Mg and Ba) and acidic (W and Nb) promoters on the activity of a 0.5 wt.%Pt/TiO_2 catalyst for the selective catalytic reduction (SCR) of NO_x using H_2 as a reductant has been systematically studied. Pronounced effects on the NO_x conversion profile were identified for the different promoters and especially on the catalyst selectivity towards nitrogen and ammonia formation. Additionally, NH_3 emissions were detected for the catalysts doped with basic promoters while NH_3 seems to be converted to N_2 via NH_3-SCR in the presence of acidic promoters.

Preferred and 2nd choice for the topic: Automotive and stationary emission control, Air cleaning and combustion
Preferred presentation: Oral preferred

Introduction and Motivations

To reduce the CO_2 emissions, the use of carbon free fuels has gained major attention during recent years. Due to its potential to improve the efficiency of internal combustion engines while reducing the emissions of harmful pollutants, hydrogen is regarded as an interesting alternative fuel for the automotive sector[1]. Herein, the use of the on-board available H_2 for NO_x removal instead of the ammonia/urea solution is an economically relevant approach[2] but very challenging. Since the direct oxidation of hydrogen at higher temperatures and the unwanted reaction pathways forming either N_2O or NH_3 instead of the desired N_2 can occur.3 For this process, noble metal-based catalysts in multicomponent systems have demonstrated a promising performance[4,5]. However, to comply with the current legislation significant improvement in their activity and selectivity is still necessary. In this context, this study reports a systematic investigation of the effect of catalyst promoters on the Pt/TiO_2 catalyst activity and selectivity.

Materials and Methods

The different catalysts were prepared by a nitrate-based precursor incipient wetness impregnation of commercial titania support to obtain the aimed promoter loadings. After drying and calcination of the doped support, the noble metal precursor was added by incipient wetness impregnation to achieve a 0.5 wt % loading of Pt. In addition, a reference catalyst with the same Pt loading without the addition of a promoter was produced. The obtained catalysts were characterized by N_2 physisorption, X-ray diffraction (XRD) and elemental analysis using inductively coupled plasma - optical emission spectroscopy (ICP-OES). Additionally, *operando* X-ray absorption spectroscopy (XAS)[6] investigations of selected samples were conducted to identify the noble metal state under reaction conditions as a function of catalyst composition. Catalytic tests for NO_x reduction were performed for the as prepared and reductively treated samples in a plug-flow reactor while analyzing the evolved gases by MS and FT-IR spectroscopy.

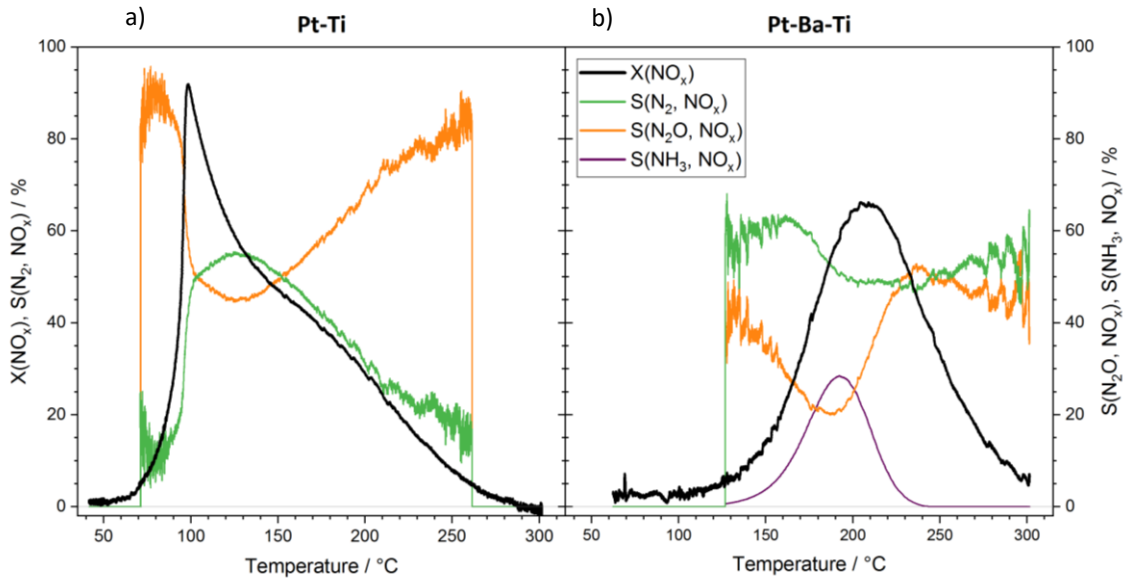


Figure 1: *Activity profiles of the plug-flow reactor tests in a gas mixture containing: 1000 ppm NO, 5000 ppm H2, 10 % O2, 5 % H2O in N2 between 50 – 300 °C (WHSV of 90.000 L*h1*gPt-1), after an oxidative treatment at 350 °C in 20 % O2 for 1 h. The conversion of NOx (black) and selectivity towards nitrogen (green), nitrous oxide (orange) and ammonia (purple) of NOx are shown line in their respective colors.*

Results and Discussion

X-ray diffraction patterns of the produced supports did not show any platinum reflexes, indicating a good distribution of small Pt particles on the titania support irrespective of the promoter type. Plug-flow reactor activity tests show a significant increase of the low temperature activity after catalyst pre-reduction, as illustrated in Figure 1 for Pt/TiO_2.

The catalysts containing basic promoters (Mg and Ba) display increased selectivity for NH_3 formation. In contrast, no NH_3 trace could be detected for the undoped catalysts and the catalysts containing acidic promoters (W and Nb). While the production of NH_3 in limited to a narrow temperature window for the Ba-promoted catalyst, nitrogen formation does not vary significantly over the whole activity range (Fig 1b). In line with the observed H_2-SCR activity profile, *operando* XAS studies and following linear combination analysis revealed a faster reduction of Pt in the tungsten promoted catalyst, while slower redox response was observed for the noble metal in the barium promoted catalysts indicating the influence of the promoters on the noble metal-support interactions.

In summary, a better understanding of the catalyst composition effects and enhancement on the H_2-SCR activity and selectivity of Pt-Ti catalysts was obtained, which enables a knowledge driven catalysts design and efficient noble metal use.

References

1. M. Ciniviz, H. Köse, *IJAET* **2012**, *1.1*, 1-15
2. G. Quing, T.W. Hamann, *et. al., Chem Rev.* **2020**, *12*, 5437-5516
3. F.J.P. Schott, S. Kureti, *et. al.*, *Appl. Catal. B: Environ.* **2009**, *87 (1-2)*, 18-29
4. M. Borchers, P. Lott, O. Deutschmann, *Ind. Eng, Chem. Res.* **2021**, *60*, 6613-6626
5. C.N. Costa, A.M. Efstathiou, *Appl. Catal. B: Environ.* **2007**, *72 (3-4)*, 240-252
6. T.J. Eldridge, J.-D. Grunwaldt, *et. al.*, *Catal. Sci. Technol.* **2024**, *14*, 4198-4210

Acknowledgements

This work was supported by Materials and Technologies for the Energy Transition (MTET) Program of the Helmholtz Association at KIT.

Design of catalysts for CO_2 hydrogenation with fine-tuned machine learning potentials

Raffaele CHEULA[1], Jonh KITCHIN[2], and Mie ANDERSEN[1]*
[1]*Aarhus University, Center for Interstellar Catalysis, 8000 Aarhus, Denmark.*
[2] *Carnegie Mellon University, Department of Chemical Engineering, 15213 Pittsburgh (PA), USA.*
**mie@phys.au.dk*

Significance and Relevance

We show the development and application of methodologies based on density functional theory and machine learning (graph Gaussian process regression and graph neural network potentials) for the modeling of surface reactions on nanoparticle catalysts. We demonstrate applications of the methodologies on CO_2 hydrogenation processes on metals, single-atom alloys, and oxide materials.

Preferred and 2nd choice for the topic: Multiscale modeling and advanced simulation aspects, CO2 utilization and recycling.
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Heterogeneous catalysis is nowadays expected to solve the challenges related to the diversification of energy sources and the reduction of greenhouse gases. The processes of CO_2 hydrogenation have the potential to sustainably produce chemicals and fuels from green hydrogen and waste CO_2 [1]. To make such processes economically advantageous, R&D in catalysis relies on the discovery and optimization of catalytic materials based on experimental testing and computational analyses. The in-silico modeling and design of catalyst materials must tackle the extreme complexity of chemical reactions at catalytic surfaces. This makes the direct application of density-functional theory (DFT) methods computationally prohibitive, especially when targeting a wide combinatory space of elements of the periodic table. This problem can be addressed with machine learning (ML) techniques, which can significantly reduce the number of DFT calculations required.

In this contribution, we apply DFT and ML models to study CO_2 hydrogenation reactions on a wide range of bi-metallic catalysts, including single-atom alloys (SAAs), i.e., materials made of single metal atoms dispersed within the surface layer of another metal. Particular attention is given to SAA materials and their ability to break the Brønsted-Evans-Polanyi relations that limit the performances of conventional catalysts.

Materials and Methods

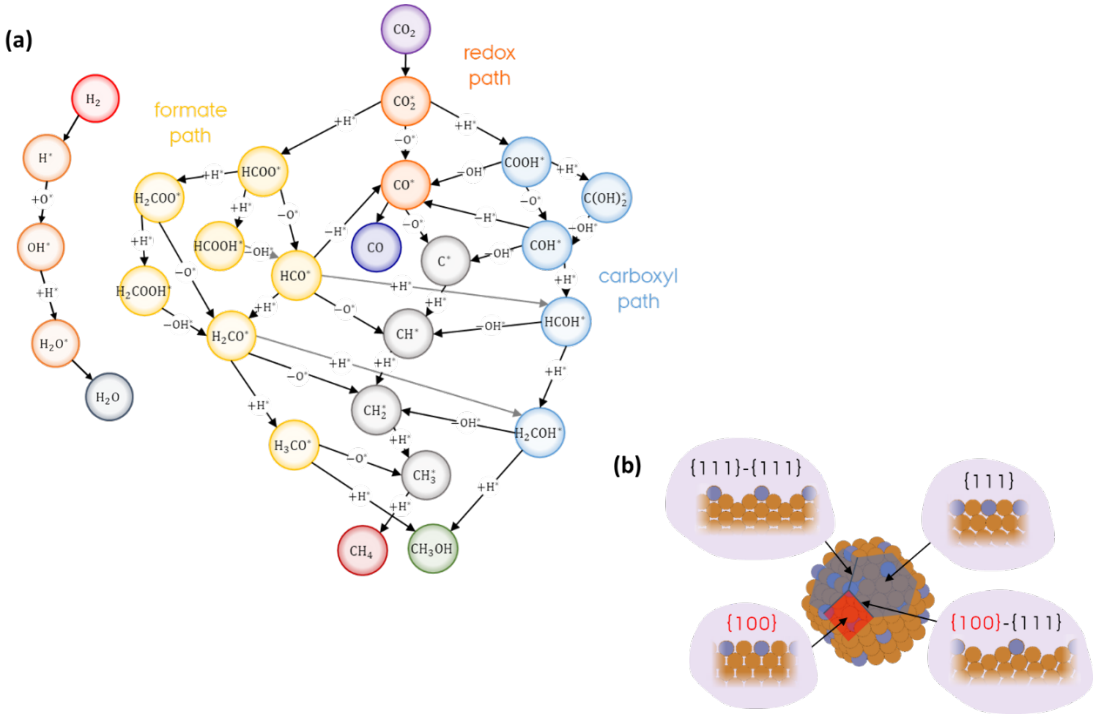
We use a graph-based Gaussian Process Regression (WWL-GPR) model [2] and machine learning potentials (MLP) from the Open Catalyst project [3-4] to calculate the adsorption energies and activation energies of the reaction mechanisms. We include in the study multiple crystal facets that catalyst nanoparticles can expose under reaction conditions. The use of pre-trained MLP models from the Open Catalyst project [4] allows us to substitute most of the DFT calculations with much faster ML evaluations in the search for minima and saddle points of the potential energy surface. Eventually, we apply structure-dependent mean-field microkinetic modeling [5] and finite differences reactor modeling to calculate the catalytic activity of the materials under investigation, accounting for the contribution of the different active sites of the catalyst nanoparticles.

Results and Discussion

The application of the framework to CO_2 hydrogenation reactions (reverse water-gas shift, methanation, and methanol production) allows us to rationalize how reaction mechanisms and catalytic performances (i.e., activity and selectivity) change with the catalyst composition, paving the way toward the design and nano-engineering of bi-metallic and SAA catalysts. On top of that, for the different materials under analysis, we evaluate the contribution of the different reaction paths

(reaction mechanism in Figure 1a) and active sites (crystal facets in Figure 1b), and we identify the energies of adsorbates and elementary steps that limit the catalytic performances of each material.

Figure 1. (a) Reaction mechanism of CO_2 hydrogenation to CO, methane, and methanol. (b) Nanoparticle shape and crystal facets considered in the study, corresponding to catalyst nanoparticles with a diameter of about 2 nm.



References

1. M.I. Alam, R. Cheula, G. Moroni, L. Nardi, M. Maestri, Cat. Sci. Tech. 11 (20), 6601-6629, 2021.
2. W. Xu, K. Reuter, M. Andersen, Nature Computational Science 2, 443–450, 2022.
3. L. Chanussot, et al., ACS Catalysis, 11, 10, 6059–6072, 2021.
4. J. Gasteiger, et al., arXiv:2204.02782, 2022.
5. R. Cheula, M. Maestri, Catalysis Today 387, 159-171, 2022.

Acknowledgements

We acknowledge support from European Union's Horizon Europe research and innovation programme under the Marie Skłodowska-Curie grant no. 101108769 and 754513. Computational support was provided by the Centre for Scientific Computing Aarhus (CSCAA) at Aarhus University.

Modeling Single-Atom Catalysis

Giovanni Di Liberto[1], Clara Saetta[1], Elisabetta Inico[1], Silvia Picello[1], Gianfranco Pacchioni[1]
[1]*Università degli Studi di Milano Bicocca, Department of Materials Science, Via Cozzi 55, Milano, Italy.*
**giovanni.diliberto@unimib.it*

Significance and Relevance

We present a computational approach to model single-atom catalysts. The approach is applied to a recently synthesized 2D material; "goldene" an Au(111) monolayer. We propose the system as a suitable support for SACs. Results indicate that SACs are stable in reaction conditions and may be active for hydrogen and oxygen evolution. Simple descriptors allow to rationalize and, in principle, to optimize the catalytic activity.

Preferred and 2nd choice for the topic: Multiscale modeling and advanced simulation aspects
Preferred presentation: Oral only.

Introduction and Motivations

Single Atom Catalysts (SACs) are emerging as new frontier in the field.[1] Computational chemistry offers a valid framework to access the atomistic details of catalytic processes and to rationalize of even predict novel systems.

In this work, the key ingredients to model SACs will be discussed. SACs differ substantially from metal surfaces and can be considered analogues of coordination compounds. In coordination chemistry, at variance with metal surfaces, stable complexes can form.[2] We show that the same can occur on SACs and their formation may change the kinetics of the process.[3,4] We propose an approach to predict the stability of SACs under working conditions of pH and applied voltage.[5] Needless to say, the adopted DFT functional affects the accuracy of the predictions, and we show evidence suggesting that self-interaction corrected schemes should be adopted.[6]

Results and Discussion

DFT numerical simulations demonstrate that these ingredients may lead to different conclusions about the activity of SACs.[7] We applied the approach to a novel candidate of supporting matrix for SACs; "*goldene*" an Au(111) monolayer (1L), recently synthesized.[8] Our results indicate that goldene-based SACs are often stable object in reaction conditions, and they may be active for relevant reactions such as hydrogen and oxygen evolution. Importantly, the activity can be rationalized and optimized by introducing simple descriptors.

This work provides an example of the important analogies between the chemistry of SACs and that of coordination compounds, and underlines the key ingredients to be accounted when attempting to provide predictions with computational frameworks. Results also point as goldene-based SACs as promising systems deserving further attention from experimental and theory communities.

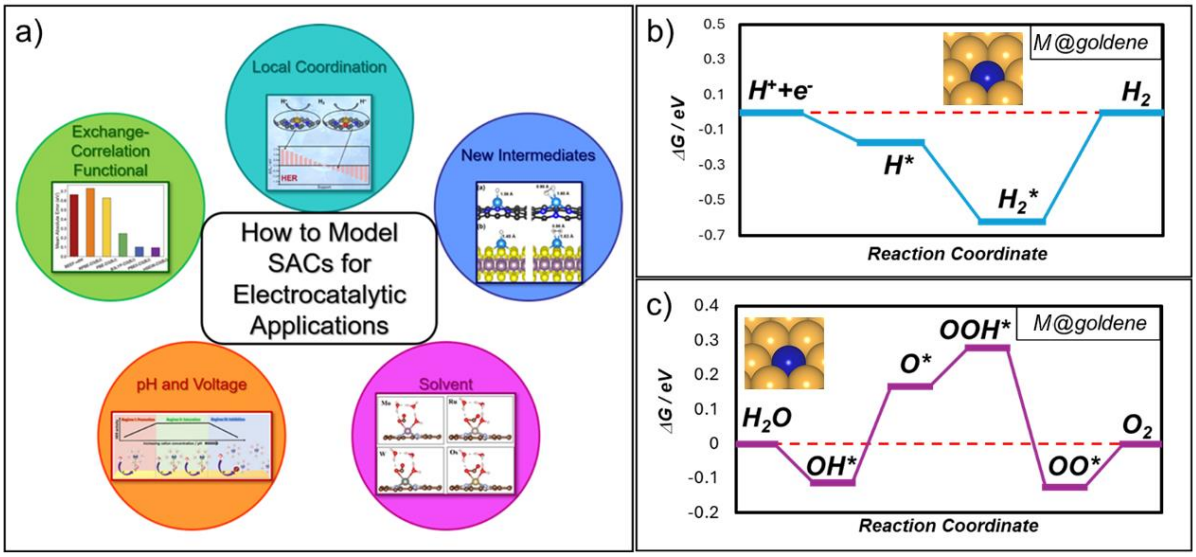


Figure 1 Key ingredients to model a SAC (panel a), reaction energy profile of HER (panel b) and OER (panel c) on Au(111)-1L based SAC.

References

1. L. Cao, Q. Luo, W. Liu, Y. Lin, X. Liu, Y. Cao, W. Zhang, Y. Wu, J. Yang, T. Yao, S. Wei, Nat. Catal. **2019**, *2*, 134.
2. G. J. Kubas, Chem. Rev. **2007**, *107*, 4152; R. H. Crabtree, Chem. Rev. **2016**, *116*, 8750.
3. G. Di Liberto, L. A. Cipriano, G. Pacchioni, J. Am. Chem. Soc. **2021**, *143*, 40321; ACS Catalysis **2022** *19*, 11682; I. Barlocco, L.A. Cipriano, G. Di Liberto, G. Pacchioni, J.Catal. **2023**, *417*, 351.
4. G. Di Liberto et al, Curr. Opin. Electrochem **2023**, 101343; J. Power. Sources **2023**, *556*, 232492; Adv. Mater. **2023**, *35*, 2307150.
5. G. Di Liberto, L. Giordano, G. Pacchioni, ACS Catalysis **2024**, *14*, 45.
6. I. Barlocco, L.A. Cipriano, G. Di Liberto, G. Pacchioni, Adv. Theo. & Simul. **2023**, *6*, 2200513.
7. C. Saetta, I. Barlocco, G. Di Liberto, G. Pacchioni, Small **2024**, *20*, 2401058.
8. Kashiwaya, Shun et al., Nature Synthesis **2024**, *3*, 744.

Beyond Linear Scaling: Innovations in Catalyst Optimization

Kihyun Shin[1]*, Hyun You Kim[2], Kyubock Lee[3]

[1]Department of Materials Science and Engineering, Hanbat National University, Daejeon 34158, Republic of Korea

[2]Department of Materials Science and Engineering, Chungnam National University, Daejeon 34134, Republic of Korea

[3]Graduate School of Energy Science and Technology, Chungnam National University, Daejeon 34134, Republic of Korea

Recent studies in electrochemical reaction simulations have revealed the construction of Volcano plots and 2D contour plots based on a strong linear scaling relation between the adsorption energies of intermediate species. This linear scaling relation provides researchers with a straightforward descriptor to predict catalyst performance and enables the visualization of large datasets of catalyst performance on simple contour plots. However, to maximize catalyst performance, it is crucial to identify outliers that do not follow the linear scaling relation. Particularly in the oxygen reduction reaction (ORR), a strong linear scaling relation between OH and OOH adsorption energies sets clear limits on catalyst activity. Overcoming these limits requires understanding how outliers arise and how researchers can control them. In this presentation, we will explore the fundamental assumptions and theories of electrochemical catalyst simulations and examine how Volcano plots and 2D contour plots are formed based on the linear scaling relation. Additionally, we will investigate the impact of ensemble, electronic, and strain effects on adsorption energies and explore various possibilities for generating outliers that deviate from the linear scaling relation.

CO-induced dynamic behavior of supported PGM nanoparticles in mild conditions

Alberto RICCHEBUONO,[1] Elena SEMINERIO,[1] Paolo LAZZARINI,[1] Eleonora VOTTERO,[1] Daniele BONAVIA,[1,2,3] Riccardo PELLEGRINI,[4] Valentina CROCELLÀ,[1] Natale Gabriele PORCARO[1] Stefano CHECCHIA,[3] Davide FERRI,[4] Andrea PIOVANO,[5] Elena GROPPO[1]

[1]*Department of Chemistry, INSTM and NIS Centre, University of Torino, via Quarello 15A, Torino, I-10135, Italy*
[2]*ESRF-The European Synchrotron, 71 avenue des Martyrs, Grenoble, 38000, France*
[3]*Paul Scherrer Institut, Forschungsstrasse 111, 5232 Villigen PSI (Switzerland)5*
[4]*Chimet SpA - Catalyst Division, Viciomaggio (Arezzo), I-52041, Italy*
[5]*Institut Laue-Langevin (ILL), 71 avenue des Martyrs, Grenoble, 38000, France*
** elena.groppo@unito.it*

Significance and Relevance

This study investigates the interaction of CO at room temperature with Platinum Group Metal (PGM) nanoparticles (NPs) supported on alumina, using gas-volumetry, adsorption microcalorimetry, and IR spectroscopy. Unique step-shaped adsorption isotherms, accompanied by an unexpected increase in the heat of adsorption, is observed for both Pd/Al_2O_3 and Pt/Al_2O_3 catalysts. This observation is correlated with a drastic change in the relative population of carbonyl species, indicating the occurrence of CO-induced surface modifications. The methodology, based on characterization techniques largely available in modern laboratories, can be extended also to PGM NPs on activated carbons, which are crucial in various industrial and environmental applications.

Preferred and 2nd choice for the topic: Fundamental advances in understanding catalysis
Preferred presentation: Oral only

Introduction and Motivations

The interaction of CO with Platinum Group Metal (PGM) nanoparticles (NPs) is a topic of wide fundamental interest and also of high practical relevance. Indeed, PGM-based systems are involved in the thermo- and electro-catalytic conversion of CO in a variety of valuable chemical compounds, and have a prominent role also in the field of hydrogen purification and pollution abatement. Last, but not least, CO is the most used probe in the characterization of Pd NPs, and it is widely adopted for a rapid and efficient evaluation of the metal dispersion through pulsed chemisorption methods. It is well assessed that CO adsorption at high temperature can cause important surface and structural modification in PGM NPs, with evident consequences on the activity and selectivity of many catalytic processes.[1-3] In contrast, the occurrence of such kind of phenomena at lower temperature is by far less documented, despite its importance for a correct interpretation of the characterization data or for understanding the behavior of Pd-based catalysts in milder condition (e.g., in electrocatalytic reactions). Identifying these environment-dependent phenomena requires a full characterization of the surface sites and of their evolution upon interaction with CO, but accessing this information is not straightforward and requires multiple in situ and operando techniques.

Materials and Methods

A series of catalysts consisting in PGM NPs supported either on alumina or on activated carbons were provided by Chimet S.p.A. Each catalyst was prepared with the metal loading of 5 wt% using the deposition-precipitation method, differing only in the metal type and support material. The catalysts were activated following a standardized protocol, involving heating under dynamic vacuum and subsequent reduction in H_2. Activation temperatures were selected based on prior H_2-TPR measurements to ensure the complete reduction of the metal oxide phase.

The CO adsorption process was monitored by coupling three complementary experimental techniques, i.e. gas-volumetry, adsorption microcalorimetry and IR spectroscopy, applied in the same

experimental conditions. Small incremental doses of CO were put in contact with the reduced catalysts in isothermal conditions until a first adsorption run was completed (primary adsorption). After a desorption step by simple evacuation of the cell, a secondary adsorption run was performed to investigate the reversibility of the process.

Results and Discussion

For the Pd/Al_2O_3 catalyst, a peculiar step in the adsorption isotherm was observed for the first time at a relative pressure corresponding approximately to 80% of the maximum coverage. This was accompanied by an unexpected increase in the heat of adsorption. Both observations were correlated with an important modification in the relative abundance of the Pd-carbonyls species, as revealed by IR spectroscopy (Figure 1). In particular, a significative increase in the amount of linear carbonyls at defective sites was detected, at the expense of bridged carbonyls.[4] These synergistic experimental observations provided an unprecedent insight into a CO-induced corrugation of the (100) surface in small supported Pd NPs. This phenomenon is driven by the strong adsorption energy of CO, which lowers the surface energy and promotes atomic rearrangement, creating new, defective and more energetic adsorption sites. Interestingly, a similar phenomenon is observed for CO adsorbed on Pt/Al2O3. Preliminary measurements suggest also a potential role of residual hydride species in affecting the CO adsorption phenomenon.

In perspective, this approach has the potential to provide a methodological benchmark in the field of characterization of adsorbate-induced phenomena in supported metal NPs on realistic catalysts of industrial and environmental relevance. It is important to notice that, while application of IR spectroscopy is restricted to samples transparent in the Mid-IR region, volumetric and micro-calorimetric measurements have no limitations and can be performed on every type of samples. This paves the way to the investigation of adsorbate-induced surface phenomena at metal NPs on activated carbons, which represent a big fraction of PGM-based catalysts employed in the chemical industry and for environmental applications.

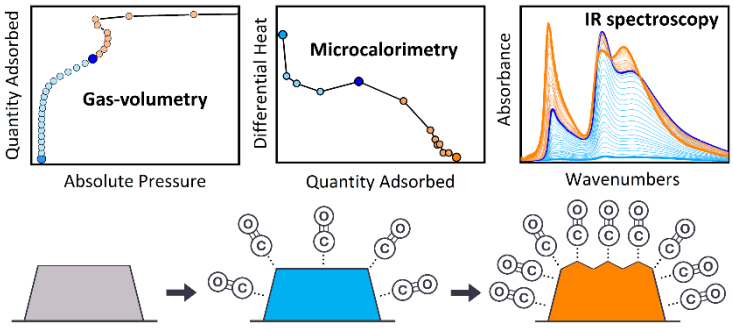


Figure 1 Combination of gas-volumetry, adsorption microcalorimetry and IR spectroscopy provided an unprecedent insight into a CO-induced surface reconstruction of Al_2O_3-supported Pd NPs involving the (100) surface and entailing the creation of new, defective, adsorption sites.

References

1. K. Murata, K., E. Eleeda, J. Ohyama, Y. Yamamoto, S. Arai, A. Satsuma, *Phys. Chem. Chem. Phys.* **2019**, *21*, 18128.
2. Jbir, J. Couble, S. Khaddar-Zine, Z. Ksibi, F. Meunier, D. Bianchi, *ACS Catal.* **2016**, *6*, 2545.
3. M. A. Newton, C. Belver-Coldeira, A. Martínez-Arias, M. Fernández-García, *Nat. Mater.* **2007**, *6*, 528.
4. A. Ricchebuono, E. Vottero, D. Bonavia, P. Lazzarini, R. Pellegrini, V. Crocellà, N. G. Porcaro, S. Checchia, D. Ferri, A. Piovano. E. Groppo, *ACS Catal.* **2024**, *14*, 13736.



Acknowledgements

We acknowledge support from the Project CH4.0 under the MUR program “Dipartimenti di Eccellenza 2023-2027” (CUP D13C22003520001).

Confining Pd on CeO_2 nano-islands for more efficient oxidation catalysts

Daria GASHNIKOVA[1], Florian MAURER[1], Maria CASAPU[1], Jan-Dierk GRUNWALDT[1,2*]
[1] *Karlsruhe Institute of Technology, Institute for Chemical Technology and Polymer Chemistry, Karlsruhe, Germany.*
[2] *Karlsruhe Institute of Technology, Institute of Catalysis Research and Technology, Karlsruhe, Germany..*
** e-mail corresponding: grunwaldt@kit.edu*

Significance and Relevance

Despite a strong interaction with the support prevents the noble metal (NM) sintering at high temperatures, this can also lead to deactivation due to the formation of highly dispersed and thus inactive species under oxidizing conditions. This study reports a novel concept for stabilizing NM clusters on ceria in low-loaded catalysts during lean operation. Complementary *in situ/operando* characterization revealed that the *in situ* formation of Pd clusters is favored by confining Pd on CeO_2 nano-islands. The proposed strategy leads to highly active and stable CO oxidation catalysts with more efficient NM usage and is attractive for further NM-catalyzed reactions.

Preferred and 2nd choice for the topic: "Automotive and stationary emission control" or "Air cleaning and combustion".

Preferred presentation: Oral preferred

Introduction and Motivations

Noble metal-based systems are crucial materials for numerous catalytic reactions including hydrogen production, synthesis of fine chemicals and emission control. Due to their unique chemical properties, the exhibited activity and stability are hardly replaceable by non-noble metal based catalysts. Considering their limited availability and high costs, a more efficient use of noble metals is desired without negative impact on the catalytic activity. In this regard, the rational design of more efficient noble metals catalysts requires a profound understanding of structure-activity correlations. Due to high structural dynamics of noble metal-based catalysts under reaction conditions, the relationship between the catalyst structure and performance can be derived only by applying complementary *in situ/operando* characterization methods.[1-5]

Besides the impact of the reaction conditions, the noble metal structure is further influenced by the interaction with the used support material. In particular, CeO_2 as a strongly interacting carrier is known to provide alternative reaction pathways due to the perimeter sites at the interface with noble metal particles [2,3] However, in oxidizing atmosphere at high temperatures this interplay also leads to the formation of isolated noble metal species, i.e. single atoms, which for Pt/CeO_2 were found to be only poorly active for CO oxidation.[2]

To overcome this effect, the surface noble metal concentration (SNMC) can be adjusted to promote the cluster formation tendency and therefore of the catalytic performance of noble metal/ceria-based materials[3]. The SNMC can be increased by applying high noble metal loadings, which is, however, not ideal. Therefore, another approach was selected in this study for regulating the noble metal state on CeO_2. By using a combination of differently interacting supports, e.g. CeO_2-nano-islands on Al_2O_3, the SNMC can be increased at a rather low noble metal loadings, as verified in our work for Pd-containing catalysts[4-5].

Materials and Methods

Pd-based catalysts (noble metal loading of 0.5 wt.%) supported on CeO_2, Al_2O_3 and 5% CeO_2-Al_2O_3 were synthesized by flame spray pyrolysis using a double nozzle configuration and palladium and aluminium acetylacetonate, and ceria ethylhexanoate as educts. For Pd/CeO_2-Al_2O_3, the Pd and CeO_2 the precursors were sprayed in one flame, separately from the Al_2O_3 precursor solution. In such a way, the preferential location on Pd on CeO_2 nano-islands could be ensured already during the catalyst preparation.

The catalytic activity of the as-prepared samples was evaluated during CO oxidation in a high excess of oxygen (1000 ppm CO/8 % O_2/N_2) in a tubular quartz reactor with an inner diameter of 8 mm. The gas composition was monitored at the reactor outlet with a Fourier transform infrared spectrometer (Multigas FTIR Spectroscopy, MKS).

To reveal differences in the evolution of Pd species during reaction and verify our approach, we performed systematic *operando* X-ray absorption spectroscopy (XAS) investigations (conducted at Pd K edge at SAMBA beamline of synchrotron radiation facility SOLEIL) and *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) studies.

Results and Discussion

The *ex situ* characterization results indicate the presence of highly dispersed species in Pd/CeO_2 and Pd/CeO_2-Al_2O_3, while small Pd nanoparticles were obtained on the weakly interacting Al_2O_3 despite the identical Pd loading of 0.5 wt.%. The synthesized catalysts showed a significantly different catalytic activity, with Pd/CeO_2-Al_2O_3 reaching the highest CO oxidation performance (temperature of 90 % conversion T_{90} = 90°C). On the contrary, Pd/CeO_2 converted only ~80 % of CO at 300 °C (Figure 1a). The complementary *in situ/operando* DRIFTS/XAS investigations revealed that the noble metal in Pd/CeO_2 remained in an almost fully oxidized state over the entire reaction range, while a slight Pd reduction was detected for Pd/CeO_2-Al_2O_3 (Figure 1b). Supported by electron microscopy data, this structural peculiarities and the high low temperature activity could be correlated with the *in situ* formation of small Pd clusters in Pd/CeO_2-Al_2O_3, confirming the proposed strategy for promoting the noble metal cluster formation and stabilization.

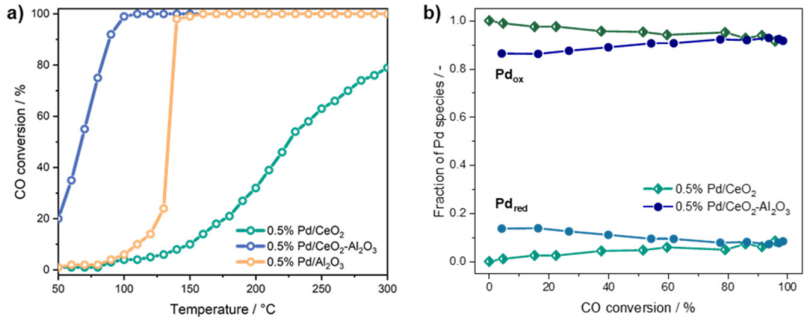


Figure 1 a) Catalytic activity of Pd-based catalysts during lean CO oxidation; b) LCA results of operando XAS spectra recorded during the CO oxidation reaction for Pd/CeO_2 and Pd/CeO_2-Al_2O_3.[4]

References

1. B. B. Sarma, J.-D. Grunwaldt, *Chimia*, **2024**, *78*, 288.
2. F. Maurer, J. Jelic, J. Wang, A. Gänzler, P. Dolcet, C. Wöll, Y. Wang, F. Studt, M. Casapu, J.-D. Grunwaldt, *Nat. Catal.* **2020**, *3*, 824.
3. F. Maurer, A. Beck, J. Jelic, W. Wang, S. Mangold, M. Stehle, D. Wang, P. Dolcet, A. M. Gänzler, C. Kübel, F. Studt, M. Casapu, J.-D. Grunwaldt, *ACS Catal.* **2022**, *12*, 2473.
4. D. Gashnikova, F. Maurer, E. Sauter, S. Bernart, J. Jelic, P. Dolcet, C. B. Maliakkal, Y. Wang, C. Wöll, F. Studt, C. Kübel, M. Casapu, J.-D. Grunwaldt, *Angew. Chem. Int. Ed.* **2024**, e202408511.
5. D. Gashnikova, F. Maurer, M. R. Bauer, S. Bernart, F. Studt, C. Kübel, C. D. Damsgaard, M. Casapu, J.-D. Grunwaldt *et al.*, *ACS Catal.* **2024**, *14*, 14871.

Acknowledgements

Daria Gashnikova acknowledges the "Fonds der Chemischen Industrie" (FCI) of the Verband der Chemischen Industrie e.V. (VCI) for financial support during her Ph.D. studies. This study was further funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – SFB 1441 – Project-ID 426888090. The authors thank the synchrotron radiation facility SOLEIL for beamtime at the ROCK and SAMBA beamlines and the KIT light source for beamtime at the CAT-ACT beamline.

Investigation on structure-activity relationship and reaction pathways of CuO/CeO_2 catalysts for NH_3 self-sustained combustion

Running Kang[1], Mingxia Yang[1,2], Zirui Zhang[1], Chenhang Zhang[1,3], Xiaokun Yi[1], Feng Bin[*1], Xiaolin Wei[1]

[1]*State Key Laboratory of High-Temperature Gas Dynamics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, PR China.*

[2] *School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, PR China.*

[3] *Key Laboratory of Beijing on Regional Air Pollution Control, Faculty of Environment and Life, Beijing University of Technology, Beijing 100124, PR China*

** Corresponding author: binfeng@imech.ac.cn*

Significance and Relevance

Catalytic combustion of high concentration NH_3 to produce N_2 and H_2O is a promising method for carbon-free fuel utilization, but is rarely reported so far. The distinct structure-activity relationship by designing CuO/CeO_2 catalysts with different CeO_2 morphologies was clearly identified. We found that NH_3 self-sustained combustion can be realized at a low NH_3 lean-combustion limit (7.6%) over Cu/Ce-Sphere at the first time. The comprehensive reaction mechanism involving intermediates transformation and contribution of different active oxygen species were revealed. These results demonstrated the viability of environmentally friendly catalytic combustors for ammonia fuel, and advanced the understanding of ammonia catalytic reaction mechanism.

Preferred and 2nd choice for the topic: Air cleaning and combustion, Fundamental advances in understanding catalysis

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Ammonia (NH_3) as a promising carbon-free fuel has attracted massive attention that aim to promote carbon peak and carbon neutrality progress. It has advantages in carbon-free footprint, high energy density, and low storage and transportation costs. However, the challenges of NH_3 utilization are its high ignition temperature and poor combustion stability and higher content of NO_x emission during direct combustion process[1]. The catalytic combustion of NH_3 to produce nitrogen (N_2) and water (H_2O) is an innovative method to solve mentioned problems, attributed to its limited NO_x production at low operating temperature, and high activity with stable combustion [2]. Intensively studies of the catalytic ammonia oxidation have been performed to remove NH_3, in situation of NH_3 is regarded as air pollutant with a low concentration (≤1%)[3,4], rather than catalytic combustion for high concentration (~10%) of NH_3 fuel. And the transition metal oxides catalysts (CuO, CeO_2, etc.) have been accepted as an alternative to noble metals, due to their low cost, excellent activity and stability[5,6]. However, the structure-activity relationship over CuO–CeO_2 catalysts remain an unresolved problem.

Therefore, this study firstly identified the distinct structure-activity relationship by designing the CuO/CeO_2 catalysts with different morphologies of CeO_2. And the combustion characteristic of high concentration (~10%) of NH_3 including self-sustained combustion limit, conversion efficiency, the wall temperature, and stability were revealed. Specifically, the detailed reaction pathways were fully discussed. These results are beneficial to make an intensive understanding of distinct structure-activity relationship and comprehensive reaction mechanism over CuO/CeO_2 for catalytic NH_3 combustion.

Materials and Methods

The nano sphere CeO_2 (Ce-S), rod CeO_2 (Ce-R) and octahedral CeO_2 (Ce-O) carriers were synthesized through a hydrothermal synthesis method. Then different CuO/CeO_2 samples were prepared with an impregnation method and denoted as Cu/Ce-S, Cu/Ce-R, and Cu/Ce-O, respectively.

Results and Discussion

The reaction activity for NH_3 catalytic ignition decreases in the subsequence of Cu/Ce-S > Cu/Ce-R > Cu/Ce-O > Ce-S, corresponding to the T_{90} (the temperature at 90% NH_3 conversion) of 220 °C, 252 °C, 287 °C, and 411 °C, respectively (Fig.1a). Compared with activity and N_2 yield of Ce-S, that of other three catalysts markedly improved, indicating the addition of CuO exhibits stronger interaction of CuO and CeO_2 and promotes the conversion of ammonia to nitrogen (Fig.1b). It is clear that the Cu/Ce-S

exhibits the highest catalytic performance, attributed to a stronger structure-activity relationship, including sphere CeO_2 with higher SSA for CuO_x dispersion, more Cu-O_x-Ce solid solution with oxygen vacancy, and stronger reducibility and oxygen mobility, etc. The NH_3 lean-combustion limits of Cu/Ce-S is 7.6% to maintain self-sustained combustion (Fig.1c). And Cu/Ce-S exhibits a remarkable performance with high NH_3 conversion (~100%) and effective N_2 yield (~98.0 %) over 360 min (Fig.1d). Such superior activity of Cu/Ce-S is attributed to the robust interaction of CuO and Ce-S (111 and 220 planes) on the oxide phases interface, reflecting the higher SSA for CuO_x dispersion to adsorb ammonia, and more Cu-O_x-Ce solid solution with oxygen vacancy (Cu^+-O_V-Ce^{3+}) to promote the active oxygen formation and mobility. The reaction mechanism for NH_3 combustion over Cu/Ce-S is also proposed. The M-K mechanism is dominant, involving the adsorbed NH_x by ammonia dehydrogenation to react with active lattice oxygen to produce N_2 and H_2O. And the L-H mechanism plays a subordinate contribution due to the formation of adsorbed HNO species. The additional *i*-SCR reaction can effectively reduce the NO formation.

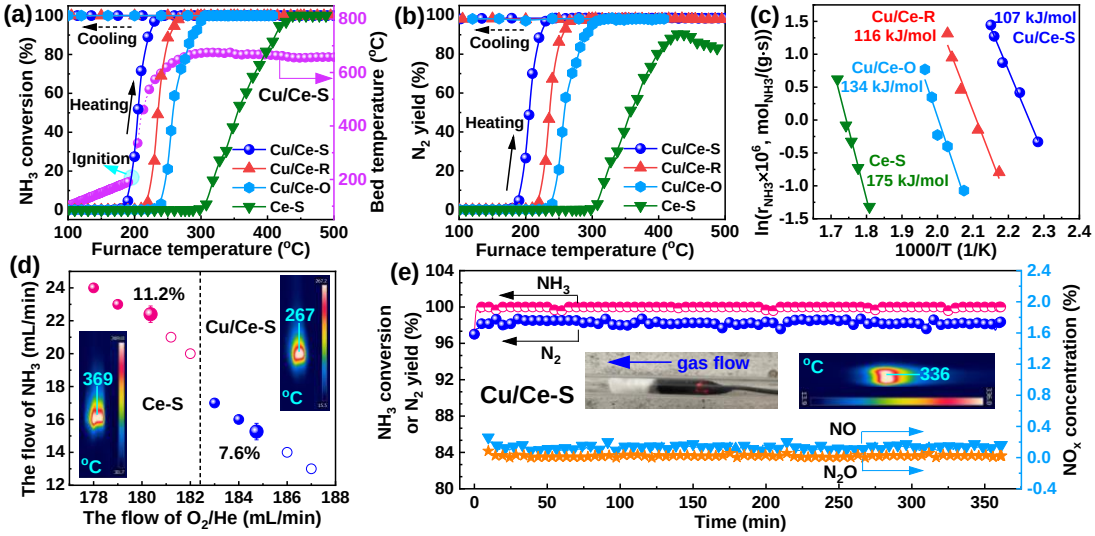


Figure 1 NH_3 conversion (a), N_2 yield (b), Arrhenius curves (c) of catalysts, lean-combustion limits (d), and stability (e) results of Cu/Ce-S under 10% NH_3+21% O_2/Ar.

References

1. H. Kobayashi, A. Hayakawa, K.D.K.A. Somarathne, E.C. Okafor, Science and technology of ammonia combustion, *Proc. Combust. Inst*. **2019**, 37, 109-133.
2. H. Liu, Y. Zhao, C.H. Zhang, Z.B. Wang, F. Bin, X.L. Wei, B.J. Dou, Evolution of reaction mechanism in the catalytic combustion of ammonia on copper-cerium mixed oxide, *J. Catal*. **2023**, 425, 20–31.
3. G.B. Liu, H.C. Sun, H. Wang, Z.P. Qu, Rational tuning towards B-sites (B = Mn, Co, Al) on CoB_2O_4 binary oxide for efficient selective catalytic oxidation of ammonia, *Chem. Eng. J*. **2023**,453, 139941.
4. Z. Wang, Z.P. Qu, X. Quan, Z. Li, H. Wang, R. Fan, Selective catalytic oxidation of ammonia to nitrogen over CuO-CeO_2 mixed oxides prepared by surfactant-templated method, *Appl. Catal. B: Environ Energ*. **2013**, 134–135, 153–166.
5. R.N. Kang, Z.R. Zhang, F. Bin, X.L. Wei, Y.D. Li, G.X. Chen, X. Tu. Catalytic ignition of CO over CuCeZr based catalysts: New insights into the support effects and reaction pathways. *Appl. Catal. B: Environ Energ*, **2023**, 327, 122435.
6. R.N. Kang, J.Q. Huang, F. Bin, Z.H. Teng, X.L. Wei, B.J. Dou, S. Kasipandi. Evolution behavior and active oxygen quantification of reaction mechanism on cube Cu_2O for CO self-sustained catalytic combustion and chemical-looping combustion. *Appl. Catal. B: Environ Energ*, **2022**, 310, 121296.

Acknowledgements

We gratefully acknowledge the financial support from the National Natural Science Foundation of China (No. 52176142, 52406171), China National Postdoctoral Program for Innovative Talents (No. BX20230380) and The Youth Fund of the State Key Laboratory of High Temperature Gas Dynamics (No.2023QN07).

Forced dynamic reactor operation for boosting the activity and selectivity of Pd-based ammonia oxidation catalysts

Camilo CÁRDENAS[1], Thomas HÄBER[2], Olaf DEUTSCHMANN[1,2], Patrick LOTT[*1]
[1]*Karlsruhe Institute of Technology (KIT), Institute for Chemical Technology and Polymer Chemistry, Engesserstr. 20, 76131, Karlsruhe, Germany.*
[2]*Karlsruhe Institute of Technology (KIT), Institute of Catalysis Research and Technology (IKFT), Hermann-von-Helmholtz-Platz 1, 76344, Eggenstein-Leopoldshafen, Germany.*
**patrick.lott@kit.edu*

Significance and Relevance

That ammonia (NH_3), which is considered a valuable C-free energy carrier, may be emitted both during direct combustion and during decomposition calls for technical solutions, i.e., selective oxidation catalysts, that selectively convert NH_3 into elemental nitrogen (N_2). This study provides spatiotemporal insights obtained during forced dynamic reactor operation of Pd-based NH_3 oxidation catalysts operated in lean conditions: Dynamic operation, i.e., introduction of rich pulses, enhances both the activity and selectivity of the Pd-based catalysts and induces gradients along the catalyst samples. The combination of noble metal-based catalysts with Fe- and Cu-zeolites further enhances the selectivity.

Preferred and 2nd choice for the topic: (1) Automotive and stationary emission control *(2)* Air cleaning and combustion.
Preferred presentation: Oral preferred.

Introduction and Motivations

Among the energy carriers that are considered feasible for large-scale decarbonization of the global energy system, ammonia (NH_3) is one of the most popular ones. In contrast to sustainable hydrogen (H_2), e.g. produced by electrolysis or pyrolysis of methane, whose transport and storage are considered challenging, the production, handling, and distribution of NH_3 can rely on established infrastructure. In addition, NH_3 has been suggested as a potent H_2 carrier, which can be decomposed into its elements or which can directly be converted into energy during combustion processes. That small amounts of NH_3 are emitted in both cases[1,2] calls for technical solutions capable of abating NH_3 emissions into the atmosphere. In this respect, the selective catalytic oxidation of ammonia (NH_3-SCO) is a viable approach to convert undesired NH_3 slippage into N_2; in fact, this technology is widely exploited already nowadays in automotive catalysis for ammonia slip catalysts (ASC).[3] While such NH_3-SCO catalysts commonly contain a noble metal, particularly platinum (Pt), which acts as oxidation functionality, also non-noble metal elements may be added as well since they have been demonstrated to exhibit great potential in suppressing the formation of undesired nitrous oxide (N_2O) as a byproduct on the one hand and to reduce the risk of NH_3 overoxidation to form nitric oxide (NO) on the other hand.[4]

While its lower activity impeded the widespread application of palladium (Pd) in NH_3-SCO catalysts, the present study demonstrates how forced dynamic reactor operation enables exploiting the unique Pd-PdO redox properties[5] for boosting the activity and selectivity of Pd-based ammonia oxidation catalysts.

Materials and Methods

After preparation of Pt- and Pd-based powder catalysts by means of incipient wetness impregnation, the materials were washcoated onto plates and monolithic substrates, respectively. Kinetic catalyst tests were conducted in lab-scale setups equipped with an FTIR spectrometer and a mass spectrometer for end-of-pipe gas analysis. In addition, spatially resolved measurements were possible: An optically accessible reactor geometry enabled obtaining spatially resolved information on selected gas phase species by applying laser-based analysis,[6] and the capillary-based spatial profiling (SpaciPro) technique implemented in a plug-flow reactor provided insights into the monolithic samples regarding temperature and species concentrations, even in more complex and realistic gas mixtures.[7]

Results and Discussion

While in light-off tests Pt-based NH_3 oxidation catalysts barely benefit from forced dynamic operation, i.e., introduction of short reducing pulses (SRP; O_2 supply cut off for 10 s) during otherwise lean operation (60 s), the conversion of NH_3 increased significantly over Pd-based samples and dynamic operation even allowed Pd-based catalysts to outperform their Pt-based counterparts. Also, the selectivity to the desired reaction product nitrogen (N_2) is enhanced substantially and although the N_2O level increases, the Pd-based catalyst in dynamic operation still outperforms the Pt-based reference catalyst. NO formation was found to an only minor extent.

The spatially resolved conversion data obtained by means of spatial profiling (SpaciPro) at T_{50} and T_{97}, i.e., the temperature of 50% and 97% NH_3 conversion, respectively, underscore the superiority of Pd/Al_2O_3 in dynamic operation compared to static operation. For instance, dynamic operation reduces T_{50} by 41°C in dry conditions (Fig. 1a) and by 53°C in humid conditions (Fig. 1b). The data obtained at T_{97} point to a pronounced shift of the reaction zone towards the inlet of the monolithic catalyst sample, both in dry (Fig. 1c) and humid (Fig. 1d) conditions. The addition of non-noble metal-based materials, namely copper- and iron-loaded zeolites, to noble metal-based ammonia oxidation catalysts can further enhance the selectivity to the desired product N_2, while suppressing NO and N_2O formation. The spatially resolved species concentration profiles suggest that double-layer washcoating is superior over zone-coating, which is assumed to originate from an intrinsic suppression of intermediate and byproduct formation along the entire length of the catalyst. Herewith, the results provide valuable guidance in designing material combinations that ensure highly efficient emission abatement.

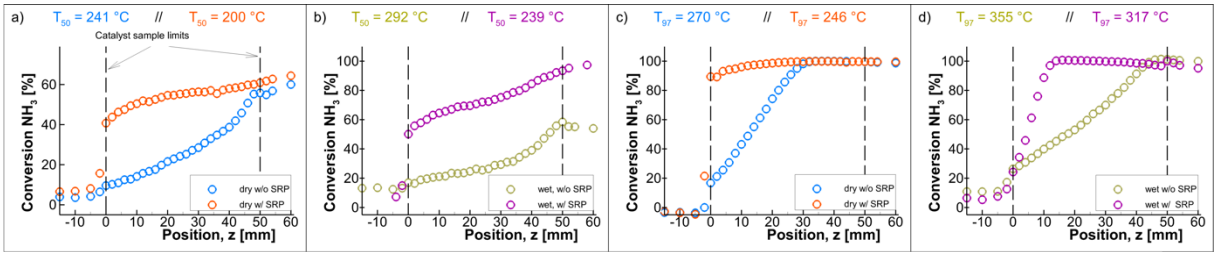


Figure 1 Spatially resolved activity data obtained for a monolithic Pd/Al_2O_3 catalyst sample in static ("w/o SRP") and dynamic SRP operation ("w/ SRP"). Gas mixture: 1000 ppm NH_3, 10 vol.% O_2 (0 vol.% for 10 s during SRP, every 60 s), 0% H_2O ("dry") or 10% H_2O ("wet"), bal. N_2.

References

1. C. Kurien, M. Mayank, *Int. J. Hydrogen Energy* **2023**, *48*, 28803.
2. I. Lucentini, X. Garcia, X. Vendrell, J. Llorca, *Ind. Eng. Chem. Res.* **2021**, *60*, 18560.
3. F. Gao, Y. Liu, Z. Sani, X. Tang, H. Yi, A. Zhao, Q. Yu, Y.J. Zhou, *Environ. Chem. Eng.* **2021**, *9*, 104575.
4. S. Shrestha, M.P. Harold, K. Kamasamudram, A. Kumar, L. Olsson, K. Leistner, *Catal. Today* **2016**, *267*, 130-144.
5. K. Keller, D. Hodonj, L. Zeh, L. Caulfield, E. Sauter, C. Wöll, O. Deutschmann, P. Lott, *Catal. Sci. Technol.* **2024**, *14*, 4142.
6. S. Wan, K. Keller, P. Lott, A.B. Shirsath, S. Tischer, T. Häber, R. Suntz, O. Deutschmann, *Catal. Sci. Technol.* **2022**, *12*, 4456.
7. K. Karinshak, P. Lott, M.P. Harold, O. Deutschmann, *ChemCatChem* **2020**, *12*, 3712.

Acknowledgements

Financial support by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) via SFB 1441, Project-ID 426888090 is gratefully acknowledged.

Spectroscopic Investigation of the Role of Water in Copper Zeolite Methane Oxidation

Dieter PLESSERS*,[1], Alexander J. HEYER[2], Jing MA[1], Augustin BRAUN[2], Hannah M. RHODA[2], Max L. BOLS[1], Robert A. SCHOONHEYDT[1], Edward I. SOLOMON[2], Bert F. SELS[1]

[1]*KU Leuven, Center for Sustainable Catalysis and Engineering, Celestijnenlaan 200F, Leuven, Belgium.*

[2] *Stanford University, Department of Chemistry, 337 Campus Drive, Stanford, U.S.A.*

** dieter.plessers@kuleuven.be*

Significance and Relevance

For the first time, a mononuclear copper site ($[CuOH]^+$) was identified as an active site for selective methane oxidation to methanol over Cu-exchanged zeolites. This active site was thoroughly characterized with a combination of site-selective spectroscopic methods (UV-Vis, resonance Raman, EPR…). Additionally, an important but contentious claim in literature stating that water can reoxidize Cu(I) in methane-reacted Cu-zeolites, has been disproven, and an alternative explanation is offered for the observed phenomena.

Preferred choice for the topic: Fundamental advances in understanding catalysis.
Preferred presentation: *Oral only.*

Introduction and Motivations

A mild, selective conversion of methane to methanol is a major goal in modern chemistry, sparking considerable interest in methane-oxidizing metal sites among heterogeneous and (bio)inorganic chemists. Cu-exchanged zeolites show promise for this direct methane-to-methanol oxidation through a typical non-catalytic, three-step cyclic process: formation of active sites at elevated temperature, methane reaction at 200°C, and methanol extraction with water (steam) at 200°C.[1,2] The extraction step, however, deactivates the material, requiring high-temperature reactivation before each subsequent methane reaction. This poses a substantial hurdle for industrial application, and thus considerable research efforts are focused on developing a catalytic process (with sufficient selectivity and yield) and on improving the efficiency and speed of the current cyclic process.

In this context, an interesting study on Cu-MOR zeolites, published in *Science* in 2017, proposed that the water/steam used for methanol extraction could simultaneously reoxidize Cu(I) to Cu(II) in the methane-reacted material.[3] Amongst other, this claim was supported by the detection of hydrogen gas during steam extraction, thought to result from water reduction. Nonetheless, the claim that water can oxidize Cu(I) remains contentious, with some authors questioning the overall reaction's thermodynamic feasibility.[4,5] This work identifies, for the first time, a mononuclear copper site ($[CuOH]^+$) as the active site for selective methane oxidation, and then investigates whether water can indeed reoxidize Cu(I) in methane-reacted Cu-MOR zeolites.

Materials and Methods

After ion exchange with copper(II) acetate and calcination, the Cu-MOR material proceeded through a three-step cycle: 1) autoreduction in helium at 500°C, 2) reaction with methane at 200°C and 3) extraction of the produced methanol with water-saturated helium (steam) at 200°C. Active site characterization and quantification after each of the 3 steps occurred via a combination of spectroscopic methods, including diffuse reflectance (DR) UV-Vis, in-situ resonance Raman, electron paramagnetic resonance (EPR), and X-ray absorption spectroscopy (XAS). Online mass spectrometry (MS) was used to analyze the gas mixture during steam extraction of the methane-reacted Cu-MOR.

Results and Discussion

First, we identified the methane-oxidizing active site in autoreduced Cu-MOR zeolites as a $[CuOH]^+$ species, characterized by a broad OH^- to Cu(II) charge transfer band at 20700 cm^{-1} in the DR-UV-Vis spectra, a $g_{\parallel} = 2.27$ feature in EPR and a Cu-O stretch of 750 cm^{-1} in resonance Raman.[6]

With the active site identified, we studied all three steps of the methane oxidation cycle (autoreduction, methane reaction, and steam extraction) using XAS and EPR to quantify Cu(I) and Cu(II)

amounts, respectively. Copper oxidation was not observed upon exposing methane-reacted Cu-MOR to steam at 200°C. Despite the lack of Cu(I) oxidation, H_2 evolution was detected during the steaming step with MS. Quantification of H_2, HD and D_2 evolution during MS isotope experiments with all four combinations of CH_4/CD_4 reaction followed by H_2O/D_2O steaming, elucidates that the hydrogen in H_2 mainly stems from the $[Cu(II)OH]^+$ active site and from methane.[7]

A plausible explanation is the decomposition of formic acid, produced from methane overoxidation over $[Cu(II)OH]^+$, into CO_2 and H_2: $HCOOH \rightarrow CO_2 + H_2$. This is supported by the near-equal amounts of CO_2 and H_2 observed with MS during steam extraction. In addition, the fraction of $[Cu(II)OH]^+$ not contributing to the measured methanol yield (and thus available for overoxidation) is around 6 times the produced CO_2/H_2 yield.[7] This corresponds to the fact that 6 equivalents of Cu(II) need to be reduced to oxidize methane to formic acid: $CH_4 + 6\ [Cu(II)OH]^+ \rightarrow HCOOH + 6\ Cu(I) + 4\ H_2O$.

In summary, we find that a mononuclear $[CuOH]^+$ is the active site for methane oxidation in autoreduced Cu-MOR. This site reduces to Cu(I) during methane reaction, after which water/steam is not able to reoxidize Cu(I) to Cu(II). The observed H_2 does not result from water reduction, but instead from formic acid decomposition after methane overoxidation.[7] The fact that water facilitates the conversion of the methane reaction products to CO_2 offers promise for the pursuit of a low-temperature oxidation process of atmospheric CH_4 to CO_2 (with a lower global warming potential) as a negative emission technology. This is an active area of research, with the most promising results so far involving a dry stream of methane and O_2 at 300°C.[8,9] Adding water could potentially lower the temperature required for complete methane oxidation, improving its feasibility for real-world applications.

References

1. B.E.R. Snyder et al. *Chem. Rev.* **2018**, *118*, 2718-2768.
2. D. Plessers, A.J. Heyer et al. *ACS Catal.* **2023**, *13*, 1906-1915.
3. V.L. Sushkevich et al. *Science* **2017**, *356*, 523-527.
4. R.A. Periana et al. Comment in *Science* **2017**, *358*.
5. J.A. Labinger et al. Comment in *Science* **2018**, *359*.
6. A.J. Heyer, D. Plessers et al. *J. Am. Chem. Soc.* **2022**, *144*, 19305-19316.
7. A.J. Heyer, J. Ma, D. Plessers et al. *J. Am. Chem. Soc.* **2024**, *146*, 21208-21213.
8. R.B. Jackson et al. *Nat. Sustain.* **2019**, *2*, 436-438.
9. R.J. Brenneis et al. *ACS Environmental Au.* **2022**, *2*, 223-231.

Acknowledgements

This work was supported by the Research Foundation - Flanders (FWO) and the National Science Foundation (NSF).

Aluminum-rich small-pore Cu-zeolites applied for NH_3-SCR of NOx

Yulong Shan*, Guangzhi He, Wenpo Shan, Yunbo Yu, Hong He
[1]*Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Haidian District, Beijing, 100085, China.*
**e-mail corresponding: ylshan@rcees.ac.cn*

Significance and Relevance

Indicate in 5-6 lines (max. 80-100 words) the main relevant results and why they are novel.

High-performance selective catalytic reduction (SCR) catalysts have garnered significant attention for the abatement of NOx emissions from both stationary and mobile sources in the past decades. The formation of dimer-Cu species, which serve as the active sites of the low-temperature SCR, relies on the mobility of Cu^I species in the channels of the Cu-SSZ-13 catalysts. We found that framework Brønsted acid sites influence the intercage diffusion and reactivity of $[Cu(NH_3)_2]^+$ complexes in Cu-SSZ-13 catalysts and provide new insights for the development of zeolite-based catalysts with excellent SCR activity by regulating the aluminum distribution by using Aluminum-rich zeolites.

Preferred and 2nd choice for the topic: Automotive and stationary emission control
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster): Oral preferred of Short Oral

Introduction and Motivations

A short description of the background and motivations.[1] Limit to a few lines, and indicate refs with an apex.[2] …….

The reaction atmosphere is capable of dynamically regulating the structure of active sites and forming active multinuclear species at low temperatures, thereby realizing quasi-homogeneous reactions over Cu-SSZ-13 zeolites in the selective catalytic reduction of NOx with NH_3 (NH_3-SCR).[1] Under the standard SCR conditions, a large number of linear $[Cu^I(NH_3)_2]^+$ complexes are generated through the coordination with NH_3 and form dimer Cu species to activate O_2 molecules, which is thought as rate-limiting step of the SCR reaction over Cu-SSZ-13.[1-3] Therefore, the dynamic characteristics of $[Cu^I(NH_3)_2]^+$ is significantly important for the low-temperature NH_3-SCR reaction. The electrostatic interaction between Cu species and the negatively charged zeolite framework Al significantly influence the $[Cu^I(NH_3)_2]^+$ mobility. However, the mechanism by which the microscopic features of the Al spatial distribution (i.e., local Al-poor or Al-rich) affect the intercage diffusion of reactive Cu species remains highly uncertain.

Results and Discussion

Describe the main scientific results and methodologies used. Add a relevant Figure that highlights the more relevant result. A final statement overviews the main conclusions and advances.

In this study,[4] the key role of framework Brønsted acid sites in the mobility of reactive Cu ions during the NH_3-SCR reaction was elucidated via a combination of density functional theory calculations, in situ impedance spectroscopy, and in situ diffuse reflectance ultraviolet-visible spectroscopy. When the number of framework Al sites decreases, the Brønsted acid sites decrease, leading to a systematic increase in the diffusion barrier for $[Cu^I(NH_3)_2]^+$ and less formation of highly reactive dimer-Cu species, which inhibits the low-temperature NH3-SCR reactivity, and vice versa. When the spatial distribution of Al sites is uneven, due to the difference in the interaction between the $[Cu^I(NH_3)_2]^+$ and the zeolite framework during the intercage diffusion of Cu species, the migration of $[Cu^I(NH_3)_2]^+$ from an Al-poor cage to an Al-rich cage (e.g., cha cage with paired Al sites) has a lower diffusion barrier, which effectively accelerates the formation of dimer-Cu species and hence promotes the SCR reaction. These findings unveil the mechanism by which framework Brønsted acid sites influence the intercage diffusion and reactivity of $[Cu^I(NH_3)_2]^+$ complexes in Cu-SSZ-13 catalysts, and provide an effective strategy for the development of zeolite-based catalysts with high-efficiency de-NOx performance.

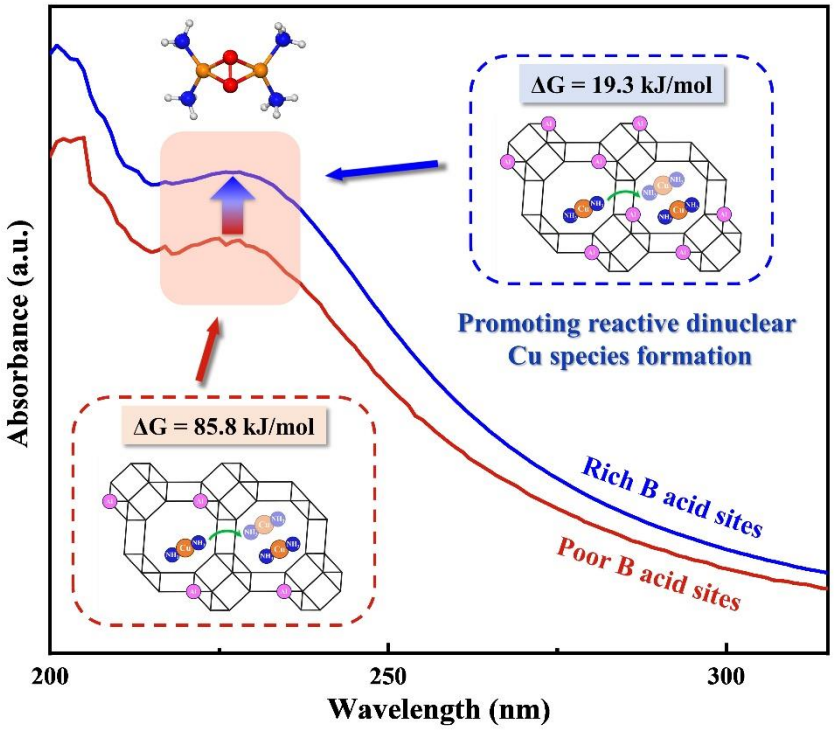


Figure 1 In situ DRUVS spectra of Cu-SSZ-13 with poor and rich Bronsted acid sites and its intercage diffusion energy barrier.

References

1. C. Paolucci, I. Khurana, A. A. Parekh et al., Science 2017, 357, 898.
2. L. Chen, H. Falsig, H. Grönbeck et al., J. Catal., 2018, 358, 179.
3. F. Gao, D. Mei, Y. Wang et al., J. Am. Chem. Soc., 2017, 139, 4935.
4. Y. Fu, W. Ding, H. Lei et al., J. Am. Chem. Soc., 2024, 146, 11141.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (22276202, 52270112, and 22188102) and the Youth Innovation Promotion Association of CAS.

The authors declare no competing financial interest.

Tuning the properties of Pt/Ni supported catalysts for the reductive amination of furfural

F. Liuzzi[1], C. Cesari[1], N. Dimitratos[1,2], S. Zacchini[1,2], S. Albonetti*[1,2]
[1] *University of Bologna, Department of Industrial Chemistry "Toso Montanari", C3 – Center for Chemical Catalysis, CIRI-FRAME, Via P. Gobetti 85, Bologna, Italy.*
** stefania.albonetti@unibo.it*

Significance and Relevance

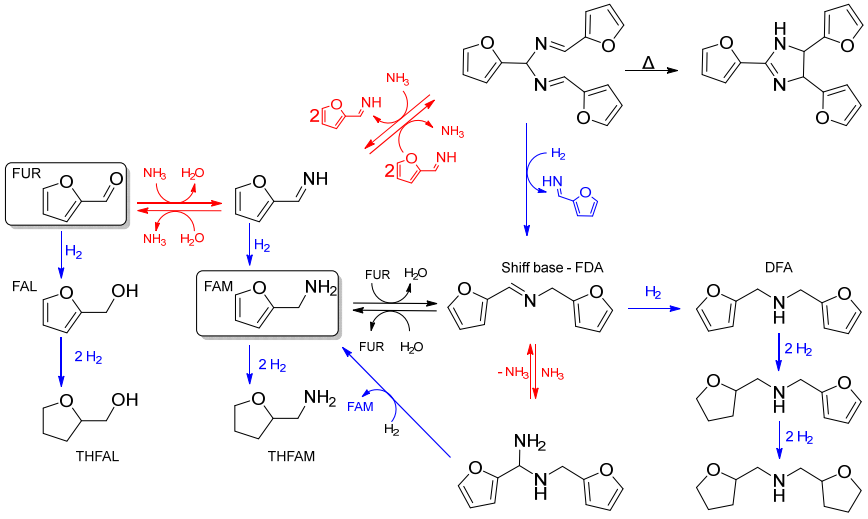
In the las years, the demand for nitrogenous compound has been increasing due to their key role in the synthesis of agrochemicals, pharmaceuticals, fine chemicals and polymers. Among the synthesis methods to produce nitrogen-containing molecules, the reductive amination reaction, using H_2 and NH_3, is the most common approach. Biomass-derived furfural (FAL) represents a promising renewable source for the preparation of amines through amination, however, obtaining satisfactory yields of amines in this reaction is challenging because side reactions like consecutive hydrogenation and self-condensation reaction cannot be ignored. Therefore, it is crucial to design and prepare catalysts with tuned hydrogenation active sites able to produce furfurylamine (FAM) in the presence of ammonia and hydrogen. Herein, this study exhibits the catalytic reductive amination of furfural to furfurylamine using well defined Pt/Ni supported catalysts synthetized from carbonyl clusters. The results highlighted the possibility of tuning the active phase to obtain very high yields of furfuryl amine in mild condition and low time of reaction.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion

Preferred presentation: Oral preferred

Introduction and Motivations

The synthesis of primary amines via reductive amination in the presence of NH_3 and H_2, as a green and sustainable process, has attracted increasing attention in the recent years. Thanks to its abundance and relatively low cost, ammonia is an interesting nitrogen source for the reductive amination of biomass-derived molecules, such as furfural, but controlling the production and selectivity of primary amine is a quite challenging aspect of this reaction [1]. Indeed, the reductive amination to primary amines has a complex mechanism, and many side reactions may occur during the process (Scheme 1). In this work, we prepared a series of Pt/Ni supported catalysts with the impregnation and decomposition of bimetallic carbonyl clusters over TiO_2, and their catalytic performances on the reductive amination of FAL to produce FAM were studied. The catalytic activity and the selectivity in the different products were correlated to the structure and surface properties of catalysts.



Scheme 1. Proposed reaction pathway for the reductive amination of furfural

Materials and Methods

A series of random alloy carbonyl clusters $[NBu_4]_2[Pt_{6-x}Ni_x(CO)_{12}]$ with different Pt:Ni molar ratios were synthesised [2] and supported on TiO_2 by wet impregnation, under nitrogen atmosphere. The final catalysts were obtained through a decomposition of the cluster under reductive atmosphere. Each catalyst was tested in the reductive amination of furfural, carrying out the reaction in a stainless-steel autoclave, in methanol, using a NH_3 solution in methanol as nitrogen source and under a pressure of H_2.

Results and Discussion

The use of bimetallic carbonyl clusters for catalysts synthesis allowed the preparation of final nanoparticle-based catalysts with precise metal composition. The synthesis of all the materials was monitored by means of FTIR spectroscopy, focusing on the vCO bands shift in the terminal and edge-bridging regions (2100 – 1700 cm^{-1}). TEM analysis on the final catalysts confirmed the formation of small nanoparticles with mean diameters around 1 nm.

The optimisation of various reaction parameters like time, temperature, H_2 pressure, and NH_3 concentration was studied with the catalyst Pt_3Ni_3/TiO_2. At the beginning of the reaction and a low temperature the main product formed were N-furfurylidenefurfurylamine (FDA), indicating that the FDA was the key intermediate of the reaction because of the high reactivity of FAM under given reaction conditions. Optimization of reaction conditions demonstrated the possibility to work in mild conditions, at 80°C and 1 h of reaction, using an excess of NH_3 respect to furfural (Figure 1A). Moreover, the study of catalyst with different Pt/Ni molar ratios (Figure 1B), showed that Ni insertion led to more selective catalysts. In particular, using Pt_2Ni_4/TiO_2 sample, complete furfural conversion and FAM selectivity higher than 90%, were obtained after one hour of reaction. In addition, the presence of nichel in Pt/TiO_2 systems was demonstrated to strongly enhance catalyst stability.

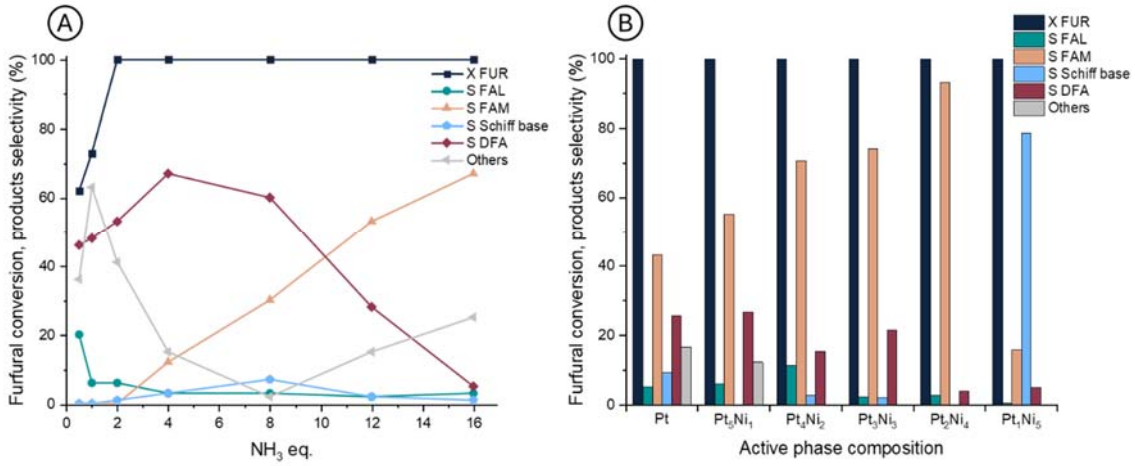


Figure 1. A) Furfural conversion and products selectivity as a function of NH_3/furfural molar ratio (reported on X axis as NH_3 equivalents) using Pt_3Ni_3/TiO_2 catalyst. B) Catalytic performances of Pt_iNi bimetallic catalysts with different Pt:Ni molar ratios. Reaction condition 80°C, 10 bar of H_2, 1 h, solvent methanol.

References

[1] N. S. Gould, H. Landfield, B.Dinkelacker, C. Brady, X. Yang, B. Xu, *ChemCatChem* **2020,** 12, 2106 – 2115.

[2] C. Cesari, B. Berti, M. Bortoluzzi, C. Femoni, M.C. Iapalucci, S. Zacchini, *Inorg. Chem.* **2021**, 60 (12), 8811–8825.

Catalytic transformation of levulinic acid and C6-carbohydrates to γ-valerolactone over Zr- and Sn-containing BEA zeolites obtained by green ultra-fast synthesis

I.I. Ivanova, R.Yu. Barakov, E. Andriako, I.A. Ermakov, A. Dubtsova
Department of Chemistry, Lomonosov Moscow State University, Leninskiye Gory 1, bld. 3, 119991 Moscow, Russia

The depletion of non-renewable carbon resources including petroleum and natural gas intensifies investigations concerning valorisation of lignocellulosic biomass into bio-fuels and value-added chemicals. Multi-stage catalytic transformation of the main components of this biomass, such as cellulose and hemicellulose, allows obtaining γ-valerolactone (GVL). This lactone has potential application as a bio-based solvent in organic reactions, an intermediate in the production of polymers and various chemicals, food additives, bio-fuels and fuel additives. The pathway of cellulose transformation to GVL includes cellulose-to-glucose hydrolysis, the dehydration of glucose to 5-hydroxymethylfurfural, hydrolysis of this aldehyde to levulinic acid and hydrogenation of acid to GVL (Fig. 1) [1]. For the individual stages of cellulose transformation to GVL, the various heterogeneous catalysts have been proposed. The stages up to obtaining levulinic acid are catalyzed by Brønsted acids, while the conversion of levulinic acids may proceeds *via* Meerwein-Ponndorf-Verley (MPV) reduction in the presence of Lewis acids and secondary alcohol as H-donor. Zr- and Sn-containing BEA zeolites are the most active and selective catalysts for the MPV reduction of levulinic acid and its esters to GVL. The high activity of these zeolites is explained by the enhanced surface area, water tolerance of their Lewis acid sites and the ability of Zr- and Sn- sites to coordinate and strongly polarise the carbonyl group of aldehyde, facilitating the transfer of two hydrogen atoms from the alcohol to a carbonyl group.

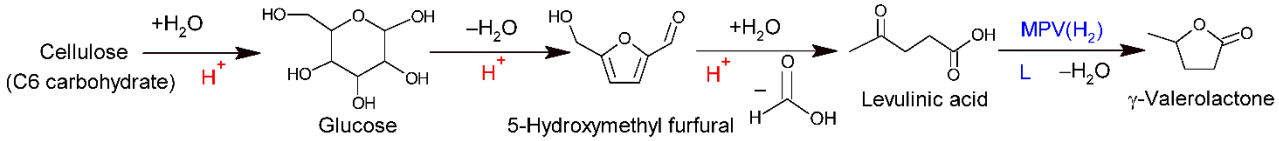


Figure 1
The reaction pathway for obtaining γ-valerolactone from cellulose over Brønsted (H^+) and Lewis (L) catalysts

The analysis of the literature data points to two mains approached used today for the Zr-BEA and Sn-BEA synthesis: 1) post-synthesis modification [2] and 2) direct hydrothermal synthesis [3]. The first approach is rather easy to accomplish, but it results on materials with large amount of defects, which prevent its application in many chemical reactions. The second procedure, based on hydrothermal synthesis leads to formation of crystals without defects. However, this procedure is rather difficult to commercialize at the industrial scale since it requires very long synthesis times and involves harmful reagents (HF). Therefore, new synthetic approaches are needed to overcome the drawbacks of existing procedures. An interesting alternative is steam-assisted crystallization (SAC). This approach allows to reduce synthesis time, use less water and template, produce less waste and increase the yield of the solid phase. Herein we report on the novel method for Zr-BEA, Zr-Al-BEA,Sn-BEA and Sn-Al-BEA synthesis based on modified SAC method and on their application in the conversion of levulinic acid, butyl levulinate and glucose into GVL.

The synthesis of Zr- and Sn-containing BEA zeolites was carried out using a new approach based on the crystallization of a wet precursor gel, which differs from the classical SAC method, in which dry gel and water are physically separated. The molar ratio of starting reagents in the wet precursor was as follows: 1 SiO_2 : x $Zr(Sn)O_2$: 0.5 TEAOH : 0.5 NH_4F : y H_2O, where x was within 0.005 – 0.008, whereas y was varied within 0.5 – 4.5. The important aspect of the developed procedure was the replacing of harmful HF as a source of fluoride ions by NH_4F.

The kinetics of crystallization at 180 °C showed that highly crystalline Zr-BEA material can be obtained already after 6 hours of crystallization, whereas in the case of Sn-BEA 37 hours was required for full crystallization, which is 25 or 7 times faster than using hydrothermal (HT) method. The crystals of the Zr – and Sn-BEA samples obtained by the SAC method had a bipyramidal octahedron shape, which is characteristic of the BEA materials obtained in a fluoride medium. However, the crystals obtained by novel

procedure were smaller (about 4-8 μm) than the crystals of the materials obtained using the HT procedure (about 11 μm).

The crystallization mechanism of Zr- and Sn-BEA in a fluoride medium was investigated using ex-situ and in-situ approaches. It has been established that at the initial stage of gel precursor preparation a solid amorphous hydrogel is formed, which has a micro-mesoporous structure. During heating of the reaction mixture, interaction of R^+ and fluoride ions with the amorphous phase occurs, which is accompained by the formation of complexes of $R^+/Si[O]_4F$ type. These complexes are precursors of crystallization and initiate the formation of zeolite nuclei. The nucleation process is rapid and begins in the early stages with almost no induction period. Further transformations occur through aggregation and densification of nucleus-containing primary structures, which is a slower process. Solid-phase reorganization of the hydrogel determines the kinetics of crystallization and crystal growth.

The number and type of active sites were determined by IR spectroscopy of adsorbed CO in the case of Zr-BEA and by IR spectroscopy of adsorbed pyridine and acetonitrile in the case of Sn-BEA. It has been established that the significant degree of Zr and Sn incorporation is achieved after 120 hours of crystallization.

The active sites of Sn-BEA, obtained by the method developed, were also studied using MAS-NMR-DP-CPMG. The spectra showed the signals of tin atoms belonging to groups I, II and III. Group I corresponds to the crystallographic positions T9, T4 and T3 in the BEA structure (–420, –425 ppm); group II — T1, T2 and T8 (–435, –437 ppm); group III — T7, T5 and T6 (–443, –447 ppm) [4].

The conversion of levulinic acid using 2-pentanol as a solvent has been investigated in the liquid phase at 115 °C under atmospheric pressure and stirring. The initial rate of GVL formation was ~ 1 $mmol_{GVL}/g_{cat}h$ in the case of Zr-Al-BEA. An even higher initial rate of 2.3 $mmol_{GVL}/g_{cat}h$ is achieved over hierarchical Zr-BEA in the conversion of butyl levulinate since this ether does not block the basic framework oxygen of active Zr–O sites, as in the case of levulinic acid.

In conclusion, the novel method of Zr- and Sn- containing BEA zeolites synthesis based on steam assisted crystallization of wet precursor was proposed. The method does not require the separation of water at the bottom of the autoclave and allows for 25 fold reduction of the synthesis time with respect to hydrothermal synthesis in the case of Zr-BEA and 7 fold reduction in the Sn-BEA. Furthermore, it leads to 5 fold increase of the product yield as compared to conventional dry gel conversion method. Finally, the important aspect of the developed procedure is the replacing of harmful HF as a source of fluoride ions by NH_4F. The resulting materials show comparable physicochemical and catalytic properties to the sample synthesized using hydrothermal crystallization.

References

[1] R. Barakov, N. Shcherban, O. Petrov, D.N. Rainer, M. Kubů, J. Čejka, M. Shamzhy, and M. Opanasenko, *Catal. Today*, **426**, 114406 (2024).
[2] P. Dapsens, C. Mondelli, and J. Pérez–Ramírez, Chem. Soc. Rev., **V. 44**, P. 7025-7043 (2015).
[3] A. Yakimov, Y. Kolyagin, S. Tolborg, P. Vennestrøm, and I. Ivanova, New J. Chem., **V. 40**, P. 4367-4374 (2016).
[4] Y. Kolyagin, A. Yakimov, Tolborg S., P. Vennestrøm, and I. Ivanova, J. Phys. Chem. Lett., **V. 9**, P. 3738–3743 (2018).

Aknowledgment

The authors thank the Russian Science Foundation for the financial support (RSF Grants No. 24-13-00103 and №24-23-00218), https://rscf.ru/project/24-13-00103 and https://rscf.ru/project/24-23-00218/.

Use of ternary Cu/Zn/La mixed oxides for the hydrogenation/hydrogenolysis of hexyl hexanoate to 1-hexanol aimed at overcoming the issues of chromium-based systems

Domenico LICURSI[1,*], Leonardo CARMASSI[1], Nicola DI FIDIO[1], Sara FULIGNATI[1], Claudia ANTONETTI[1], Anna Maria RASPOLLI GALLETTI[1]

[1]*University of Pisa, Department of Chemistry & Industrial Chemistry, Via Giuseppe Moruzzi, 13, Pisa, Italy.*

** domenico.licursi@unipi.it*

Significance and Relevance

Cu-based catalysts are really attractive for the hydrogenation/hydrogenolysis of the esters to the corresponding alcohols, given their low cost and robustness, which make them already attractive for the methanol synthesis. In this work, hexyl hexanoate (HexHex) hydrogenolysis to 1-hexanol (HexOH) with different Cu-based catalysts was studied, e.g. binary Cu/Zn and ternary Cu/Zn/La catalyst mixed-oxides. For these evaluations, Cu/Zn/Cr mixed oxides were considered as benchmarks for the catalytic evaluations of our Cr-free catalysts. It was found that lanthanum effectively acted as a promoter, helping to improve the activity of the Cu active metal, and reducing the sinterization issue (35 mol% of conversion for the Cu/Zn versus 90 mol% for the Cu/Zn/La, working under the best reaction conditions). The catalytic performances of the Cu/Zn/La catalyst are comparable with those of the ternary Cu/Zn/Cr system (91 mol%), working under the same best reaction conditions, thus confirming the possibility of using our Cr-free catalytic systems for improving the sustainability of the HexOH synthesis.

Preferred and 2nd choice for the topic: (preferred topic) Green chemistry and biomass transformation, renewable resources conversion; (2nd choice) Fundamental advances in understanding catalysis. *Preferred presentation*: Oral only.

Introduction and Motivations

Hydrogenation/hydrogenolysis of esters to the corresponding alcohols is industrially attractive, given the relevance of these latter for the production of jet-fuels, diesel additives, lubricants and plasticisers. [1] The first catalyst employed for this reaction was copper chromite ($CuCr_2O_4$, Adkins catalyst), which is prone to give Cr^{6+}, nowadays undoubtedly recognized for its toxicity to the man and environment. To overcome this relevant issue, several Cr-free catalysts have been developed over the past years, mainly based on noble metals, such as Pt, Re, Pd and Ru, showing high catalytic activity towards the hydrogenation of medium-chain esters (C_4-C_8) to the corresponding alcohols. [2] Anyway, the high cost of these noble-based catalysts makes difficult their further use on the industrial scale, a bottleneck that shifts the attention towards the development of new, cheaper non-noble catalysts, in particular those based on Ni, Co and Cu metals. Regarding the Cu-based ones, binary Cu-Zn-mixed oxides are effective towards the hydrogenation of esters, Cu representing the active species, whilst ZnO stabilises Cu, reducing its sintering, at the same time affecting the acid-base properties of the bulk catalyst.[2]In this work, a ternary Cu/Zn/La catalyst, which was proposed by us for the methanol synthesis reaction from alkyl formates[3], has been now proposed for the hydrogenation/hydrogenolysis of HexHex to HexOH. Lanthanum acts as a promoter, further improving the resistance to sintering, at the same time affecting the acid-base properties of the bulk catalyst, both factors that synergistically play a key role in the involved reaction mechanism. [4]

Materials and Methods

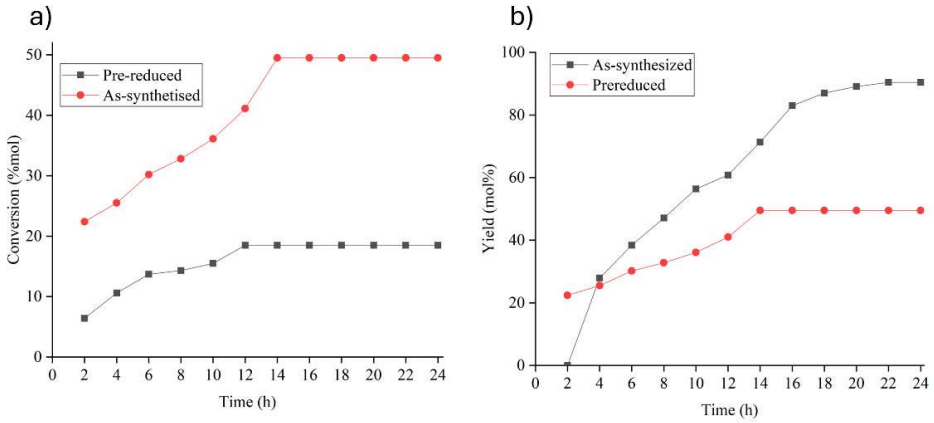
The syntheses of the Cu/Zn/Cr, Cu/Zn and Cu/Zn/La catalysts were carried out by co-precipitation technique, according to the detailed procedures available in the literature. [3,5] The corresponding compositions were confirmed by the Inductively Coupled Plasma (ICP) spectroscopy technique. Hydrogenation reactions were carried out in a 300 mL stainless steel Parr 4560 autoclave, equipped with a P.I.D. controller (4848). The analytical determinations were performed by GC-FID

analysis, using a DANI GC1000 DPC gas chromatograph. Further analytical details are reported in a previous work of us. [6]

Results and Discussion

First, Cu/Zn/Cr catalyst was tested for the hydrogenolysis reaction of model HexHex (pH_2: 100 bar, T: 230 °C, catalyst loading 5 wt%), monitoring the kinetics for 24h, whereas the corresponding HexHex conversion of 82.6 mol% was obtained. In the attempt of improving to the best the activity of the pristine catalyst, a wet pre-reduction step was included (pH_2= 100 bar, time: 5h, T: 200 °C in MeOH). [5] In this case, only a moderate improvement of the conversion was achieved (92 mol% after 24 h), always keeping the complete selectivity to HexOH. Then, the Cu/Zn-based catalyst was tested, working under the same reaction conditions, ascertaining a much lower conversion (35 mol%), which was stable already after 6h of reaction, demonstrating the unsatisfactory performances of this binary system towards HexOH production. Instead, the Cu/Zn/La catalyst allowed a much higher conversion (about 90 mol% after 24 h), demonstrating the positive effect of lanthanum towards the reduction of copper sintering, at the same time affecting the acid-base properties of the bulk catalyst, both factors that synergistically play a key role in the involved reaction mechanism. [4] Remarkably, a worsening of the HexHex conversion was ascertained by including the pre-reduction step of the ternary catalyst (only 50 mol% after 24 h, see Figure 1), highlighting that excessive reduction of the Cu species is not effective for the hydrogenolysis stage. [7] Further characterizations of all pristine and spent catalysts are in progress, to deepen the role of metal oxidation state and acidity/basicity of the species involved in the reaction mechanism.

Figure 1 Kinetics of HexHex hydrogenation to HexOH using as-synthesized and pre-reduced Cu/Zn (1a) and Cu/Zn/La (1b) catalysts.



References

1. M. He, M. Wang, G. Tang, Y. Fang, T. Tan *Applied Catalysis A General* **2018***, 550*, 160-167
2. O. Kikhtyanin, J. Aubrecht, V. Pospelova, D. Kubička *Catalysts,* **2021**, *11*
3. G. Braca, A. M. Raspolli Galletti, N. J. Laniyonu, G. Sbrana, E. Micheli, M. Di Girolamo, M. Marchionna *Ind. Eng. Chem. Res.* **1995**, *34*
4. H. Song, A. Fazeli, H. Kim, A. Eslami, Y. Noh, N. Saeidabad, D. Moon *Fuel* **2021** *283*
5. G. Busca, M.E. Patuelli, F. Trifirò , A. Vaccari Structure and Reactivity of Surfaces **1989**
6. D. Licursi, A. M. Raspolli Galletti, C. Antonetti, G. A. Martinez, E. Jones, L. Bertin, N. Di Fidio, S. Fulignati, G. Pasini, S. Frigo, *Catalysts* **2022,** *12*, 1550
7. S. Li, Y. Wang, J. Zhang, S. Wang, Y. Xu, Y. Zhao, X. Ma **2015** *Ind. Eng. Chem. Res*., 54

Acknowledgements

The authors thank the PRIN 2022-Project REFIL “Renewable liquid Fuel of new generation from wastewater sludge: a step towards circular economy” (Progetti di Ricerca di Rilevante Interesse Nazionale – Bando 2022 - 2022KA5WL8).

Transfer Hydrogenation of Furfural Under Continuous Flow Conditions by Shvo Catalyst

Maitê CAMPOS[1], Luís ADRIANO SANTOS DO NASCIMENTO[1], Emilia PAONE[2], Giulia BRUFANI[2,3], Chiara LENZI[4], Andrea PIAZZI[4], Rita MAZZONI[4], Luigi VACCARO[3], Francesco MAURIELLO[*,2]

[1]*Universidade Federal do Pará UFPA, Department of Biotechnology, Augusto Corrêa Street, Belém, Brazil.*

[2] *Dipartimento DICEAM, Università degli Studi Mediterranea di Reggio Calabria, Via Zehender, Reggio di Calabria, Italy.*

[3] *Dipartimento di Chimica Biologia e Biotecnologie, Università degli Studi di Perugia, Via Elce di Sotto 8, Perugia*

[4] *Dipartimento di Chimica Industriale, Università degli Studi Alma Mater Studiorum di Bologna, Viale Risorgimento 4, Bologna, Italy.*

** francesco.mauriello@unirc.it*

Significance and Relevance

This study introduces the first-ever application of the Shvo catalyst in continuous-flow conditions for the transfer hydrogenation of furfural to furfuryl alcohol. Achieving a conversion rate of 94.1%, this method represents a substantial improvement in safety, efficiency, and sustainability over traditional batch processes.

Preferred and 2nd choice for the topic: "Green chemistry and biomass transformation, renewable resources conversion"
Preferred presentation: Oral only

Introduction and Motivations

Furfural is a cornerstone biomass-derived platform chemical with numerous industrial applications [1-2]. Traditional hydrogenation techniques, employing molecular hydrogen in batch reactors, face several limitations, including high pressure requirements and harsh reaction conditions. Addressing these challenges, our research utilizes the Shvo catalyst [3], a renowned ruthenium-based complex, in a continuous-flow system for the catalytic transfer hydrogenation (CTH) of furfural [4]. This approach not only circumvents the drawbacks of batch processing but also enhances reaction efficiency and safety. Significantly, this study represents the first implementation of the Shvo catalyst in continuous-flow conditions in the reduction of furfural, promoting an efficient, safer and more sustainable approach for transfer hydrogenation process of biomass derived molecules.

Results and Discussion

Our study successfully implemented the Shvo catalyst in a continuous-flow system for the transfer hydrogenation of furfural to furfuryl alcohol, achieving a high conversion rate of 94.1% under optimized conditions (150°C, a flow rate of 250 µL/min, and 1.5 equivalents of 2-propanol). These conditions were meticulously fine-tuned to balance efficiency, sustainability, and cost-effectiveness. The use of 2-methyloxolane (MeOx) as a co-solvent played a pivotal role in enhancing the solubility of the Shvo catalyst, facilitating its applicability under continuous flow conditions. The exceptional selectivity of the Shvo catalyst in the transfer hydrogenation of furfural into furfuryl alcohol was highlighted by the absence of etherification, acetalization, or other unwanted pathways, even under varied experimental conditions. While 2-propanol provided the highest conversion rates, experiments with ethanol and methanol showcased lower efficiencies, underscoring the importance of selecting an appropriate hydrogen donor for maximizing yield and selectivity.

Varying the equivalents of 2-propanol demonstrated a clear trend: higher equivalents generally improved the conversion efficiency. At 90°C, increasing the isopropanol from 1.0 to 1.5 equivalents resulted in an increase from 80.1% to 85.2% in furfural conversion. This trend was consistent across all tested temperatures, peaking at 97.4% conversion at 150°C with 1.5 equivalents of isopropanol (Figure 1). These results illustrate the importance of hydrogen donor availability in optimizing the catalytic process, highlighting a crucial factor in the design of continuous-flow chemical reactions.

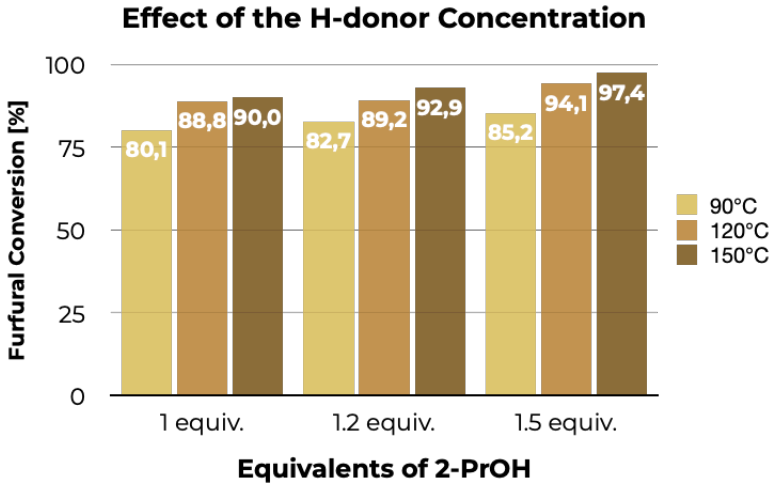


Figure 1 Effect of Hydrogen Donor Concentration (1.0, 1.2, and 1.5 equivalents of 2-PrOH) on the Conversion Efficiency of Furfural at Temperatures of 90°C, 120°C, and 150°C.

After completing the transfer hydrogenation reaction, the Shvo catalyst can be easily recovered by a simple process of precipitation into hexane. This method effectively separates the catalyst from the reaction mixture, allowing it to be collected and reused after a proper regenerative process. Our studies have demonstrated that the Shvo catalyst maintains a high level of activity even after five cycles of reuse, with minimal degradation in performance.

The study also focused on green chemistry metrics to evaluate the environmental impact of the reaction system. The atom economy (AE) was calculated at 0.63, indicating moderate efficiency in using reactant atoms towards the desired product. The reaction mass efficiency (RME) stood at 0.34, reflecting the challenge of balancing reactant use with desired output but also highlighting areas for process improvement. The E-factor, which measures waste production relative to the product, was 1.9, demonstrating a relatively low level of waste generation. These metrics underscore the sustainable nature of the process, suggesting that while there is room for improvement, the system offers significant environmental benefits compared to traditional batch methods.

Finally, in order to extend the substrate scope, transfer hydrogenations of other aldehydes and ketones were also tested, confirming the applicability of this process to a broad range of substrates.

In conclusion, this research not only confirms the viability of the Shvo catalyst for continuous-flow applications but also emphasizes its potential for industrial-scale sustainable chemical synthesis, marking a significant advancement in the field of green chemistry.

References

1. M. Besson, P. Gallezot, C. Pinel, *Chem. Rev*. **2014**, *114*, 1827–1870.
2. C. Xu, E. Paone, D. Rodríguez-Padrón, R. Luque, F. Mauriello, *Chem. Soc. Rev*. **2020**, *49*, 4273–4306.
3. B. L. Conley, M. K. Pennington-Boggio, E. Boz, T. J. Williams, *Chem. Rev*. **2010**, *110*, 2294–2312.
4. M. J. Gilkey, B. Xu, *ACS Catal*. **2016**, *6*, 1420–1436.

Acknowledgements

This work has been funded by the European Union – NextGenerationEU under the Italian Ministry of University and Research (MUR) within PNNR MUR - M4C2 - Investimento 1.5 - "Ecosistemi dell'Innovazione". In particular, authors thanks projects “Ecosistema TECH4YOU”, “Ecostistema ECOSISTER” and “Ecosistema VINITALY”.

Guaiacol hydrodeoxygenation over Ni-Fe supported on Nb_2O_5 and SiO_2 catalysts

Karen Lucia P. Pantoja[1], Naiara da Costa Telis[1,2], Gisele Cristina R. Silva[1], Klaus Raffelt[2], Ricardo R. Soares[1,*]
[1]*Faculty of Chemical Engineering, Federal University of Uberlândia, Uberlândia, Minas Gerais, Brazil*
[2]*Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1. Eggenstein-Leopoldshafen*
** e-mail : rrsoares@ufu.br*

Significance and Relevance

Bio-oil upgrading is one of the key processes for enabling drop-in biofuel production by co-processing or BTL technologies. This contribution will help with the development of active, stable, and selective catalysts for bio-oil upgrading and/or *ex-situ* catalytic fast pyrolysis. The Nb_2O_5-supported catalysts developed in this work demonstrate to be efficient in the HDO reaction in both gas and liquid phases.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion
Preferred presentation: Oral preferred

Introduction and Motivations

The conversion of biomass in fuel is being considered a potential process for generation of sustainable energy. Fast pyrolysis of biomass produces bio-oil, which has to upgrade due to its high viscosity, corrosiveness, low heating value, high water content, and thermal instability of components [1]. Hydrodeoxygenation (HDO) is one of the available upgrading routes, which occurs in the presence of a solid catalyst and hydrogen as reactant at moderate temperature (300-600°C) [2]. Previous studies revealed the optimum thermodynamic condition [3] and the high stability and selectivity towards phenol in the HDO of guaiacol, a model compound representative of bio-oils derived from lignin, over Pt/Nb_2O_5 catalyst. This study reports the reaction over $Ni\text{-}Fe/Nb_2O_5$. Data were also collected for reactions over a traditional support, SiO2, for comparison

Materials and Methods

Niobium acid (HY-340/CBMM) and SiO_2 (AEROSIL-50, Degussa) were calcined at 773 K during 4 h to produce the supports Nb_2O_5 and SiO_2. Monometallic (5 wt. % Ni or 2 wt.% Fe) and bimetallic (5 wt. % Ni and 2 wt.% Fe) catalysts were prepared by incipient wetness impregnation of the supports with an aqueous solution of $Ni(NO_3)_2.6H_2O$ and/or $Fe(NO_3)_2$. The samples were characterized by TPR, UV-Vis, X-ray diffraction (XRD), N_2 physisorption, and H_2-TPD. HDO of guaiacol catalytic tests were carried out in a fix-bed glass reactor at atmospheric pressure and vapor phase at conditions without mass transfer restrictions.

Results and Discussion

All the catalysts exhibited good stability after 50 hours on-stream, figure 1. The monometallic catalysts supported on Nb_2O_5 had their activities higher than the SiO_2-supported ones. The synergism between Ni or Fe and NbOx species probably enables oxophilic sites formation which enhances direct deoxygenation (DDO) reactions, since the main products observed in Table 1 are formed by them [3]. Moreover, over iron the DDO reaction towards phenol was higher with the Nb_2O_5 than SiO_2, while over nickel the formation of veratrole was enhanced. On the other hand, the selectivity has not changed when over the bimetallic catalysts. However, it was remarkable that the bimetallic catalysts activities were higher than the monometallic ones, which denotes a synergism between the metal

phases over both supports. This result is due to the new sites formation as indicated by the TPR, UV-Vis and H_2-TPD results.

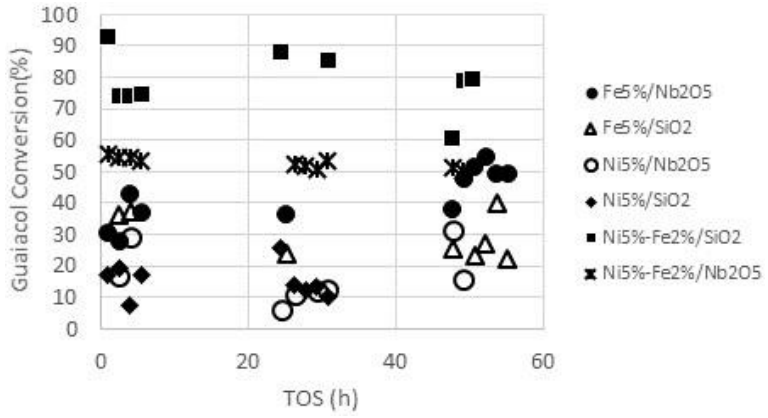


Figure 1. Gas-phase guaiacol HDO (H_2/Guaiacol = 8) at 300 °C and atmospheric pressure over the Ni-Fe supported catalysts**.**

Table 1. Guaiacol conversion and selectivity after 50 hs. TOS – HDO (300 °C, 1 bar)

Catalyst	**Guaiacol Conv.(%)**	**Selectivity (%)**			
		Phenol	**Catechol**	**o-Cresol**	**Veratrol**
Ni5%/SiO_2	10.1	53.5	14.1	22.9	9.5
Ni5%/Nb_2O_5	23.5	49.9	6.2	25.2	19.0
Fe5%/SiO_2	22.4	49.3	13.5	20.6	16.6
Fe5%/Nb_2O_5	49.6	55.8	10.8	18.2	15.4
Ni5%-Fe2%/SiO_2	79.6	66.3	7.1	14.8	11.8
Ni5%-Fe2%/Nb_2O_5	50.3	60.1	9.3	15.5	15.1

Acknowledgements
This work was supported by CNPq, CAPES, PETROBRAS, EMBRAER, SUZANO, KLABIN and FAPEMIG,

References

1. Huber, G.W., Iborra, S., and Corma, A.. *Chem. Rev*. 106, 4044 (2006).
2. Bu, Q., Bu, Lei, H., Zacher, A.H., Wang, L., Ren, S., Liang J., Wei, Y., Liu, Y., Tang, J., Zhang, Q., Ruan, R. *Bioresour. Technol.* 124, 470 (2012).
3. Silva, N.K.G., Ribas, R.M., Monteiro, R.S., Barrozo, M.A.S., Soares, R.R. *Renewable Energy,* 2020.

Vegetable oil-based 5-membered cyclic carbonates as bio-based building blocks for NIPU foams: catalysis, synthesis and kinetic aspects

Martino DI SERIO*[,1], Federica ORABONA[1,2], Tapio SALMI[1,2], Vincenzo RUSSO[1,2]

[1]*Università di Napoli 'Federico II', Chemical Sciences, IT-80125 Napoli, Italy*
[2]*Åbo Akademi, Laboratory of Industrial Chemistry and Reaction Engineering (TKR), FI-20500 Turku/Åbo, Finland*
**martino.diserio@unina.it*

Significance and Relevance

In this work, the catalyzed CO_2 cycloaddition of epoxidized soybean oil (ESBO) to produce 5-membered cyclic carbonates has been studied from the catalytic and kinetic point of view. The reaction product, i.e. carbonated soybean oil epoxy (CSBO) has been successfully utilized in the aminolysis reaction with a bio-based diamine for the synthesis of fully renewable isocyanate-free polyurethane foams (NIPU) through a self-blowing approach.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, CO_2 utilization and recycling
Preferred presentation: Oral preferred

Introduction and Motivations

Globally, agricultural waste deriving from e.g., agro-industries, crop residues and livestock accounts for approximately 2 billion tons per year. The valorization of this huge amount of biomass is indeed extremely urgent in the circular economy viewpoint. For instance, vegetable oils can be readily extracted by decomposition and further treatment of biomass and utilized as feedstock for the production of value-added products, such as biopolymers and biopolymers building blocks[1]. In particular, epoxidized vegetable oils i.e., soybean oil epoxy (ESBO), are promising precursors for the synthesis of non-isocyanate polyurethanes (NIPU). The catalysed cycloaddition of CO_2 to ESBO produces a multifunctional five-membered cyclic carbonate i.e., soybean oil cyclic carbonate (CSBO) which is particularly interesting as the precursor of NIPU[2].
In this work, the carbonation of ESBO was performed in a stainless-steel reactor autoclave (Parr) under solvent-free conditions, at relatively high temperatures and CO_2 pressures and in the presence of quaternary ammonium salt halides as catalysts. The kinetics of the reaction has been studied by varying the operating parameters i.e., temperature, pressure and catalyst load, and the final product has been further utilized to synthesize non-isocyanate polyurethane (NIPU) foams with the self-blowing approach.

Materials and Methods

The soybean oil epoxy (ESBO) has been fully characterized by IR and GC-MS to determine the fatty acids content. The carbonation of ESBO was performed in a stainless-steel reactor autoclave (Parr) in solvent-free mode, at relatively high temperature and pressure of CO_2 and in the presence of quaternary ammonium salt halides. In particular, tetrabutylammonium bromide, chloride and iodide (TBAB, TBAC, TBAI) were tested and compared. Very precise kinetic studies were conducted with the best catalyst by varying the reaction temperature (80-130 °C), CO_2 pressure (10-30 bar), catalyst loading (2.5-10 wt%) and stirring rate (200-500 rpm). The reaction products were analyzed both qualitatively and quantitatively with ^{1}H-NMR 500 MHz employing $CDCl_3$ as solvent, after careful validation of the analytical method by comparison with the well-established Jay's oxirane titration[3].
At the end of the reaction, the catalyst was separated from the product by solvent extraction with ethyl acetate and water. Finally, ethyl acetate was separated in the rotavapor at approximately 65 °C, 100 mbar and 50 rpm. The final product CSBO was then reacted with 1,4-diaminobutane together with suitable catalysts/fillers to successfully obtain NIPU foams.

Results and Discussion

The kinetic experiments were conducted with tetrabutylammonium chloride (TBAB) as the catalyst, being the most active among the ones screened. The conversion of the soybean oil epoxy (ESBO) and the yield of the cyclic carbonate (CSBO) were measured by quantitative ^{1}H-NMR. The conversion results were then compared with titration of the epoxy group in order to validate the analytical method. Both techniques confirmed the full conversion of ESBO after 24 h of reaction at 130°C and 40 bar from the disappearance of epoxy peaks in the area 2.8-3.2 ppm (Figure 1). In the same conditions, IR measurements confirmed once again the full conversion of the ESBO since the peak in the region 815-950 cm^{-1} (C-O-C stretching of oxiranes) disappeared after the carbonation experiment. At the same time, the production of the CSBO was confirmed by the appearance of a band at 1800 cm^{-1}. Regarding the yield of CSBO, it was overall higher than 80-90%; however, the formation of keto-byproducts was observed in the NMR spectra at 2.4 ppm and it occurred through a parallel reaction network respect to the main reaction. As revealed by the kinetic experiments, the reaction temperature and the catalyst amount had a strong influence on both the reactant conversion and the product yield, while CO_2 pressure had overall a milder effect on the system. After separation of the catalyst by liquid-liquid extraction, pure CSBO was obtained and then mixed with 1,4-diaminobutane (putrescine) to obtain NIPU foams. Different formulations were tested varying the starting material/fillers kind and amounts. It was observed that blending CSBO with another bio-based cyclocarbonate i.e., butanediol bis(cyclocarbonate) (BCC) resulted in the best performance of the final material thanks to the presence of unsubstituted methylene groups. The resulting NIPU foams were thermally, chemically, and morphologically characterized.

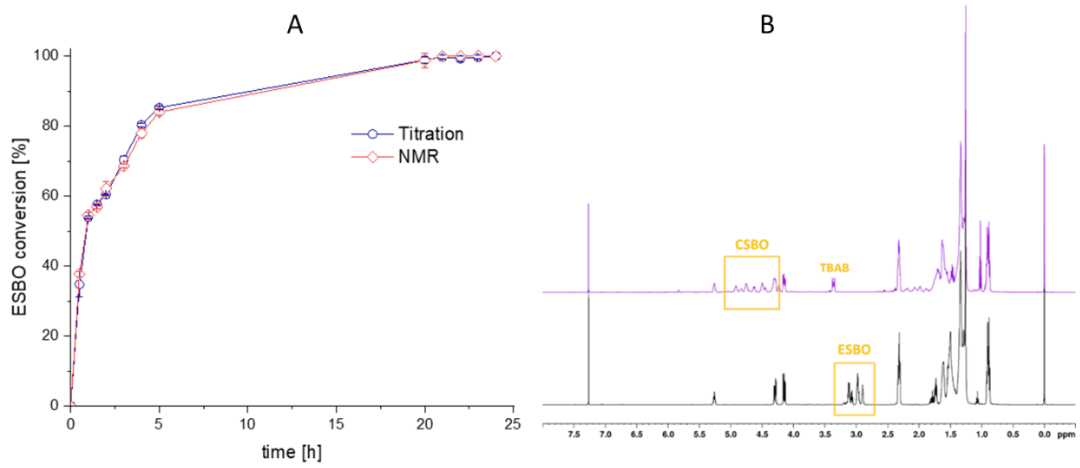


Figure 1. Reaction scheme of limonene dioxide carbonation (A). Temperature effect on the kinetics of CO_2 cycloaddition of limonene diepoxide (B).

References

1. R. Singh, R. Das, S. Sangwan, B. Rohatgi, R. Khanam, S.K.P.G. Peera, S. Das, Y.A. Lyngdoh, S. Langyan, A. Shukla, M. Shrivastava, S. Misra, Environmental Sustainability. 4 (2021) 619–636.
2. W.Y. Perez-Sena, K. Eränen, N. Kumar, L. Estel, S. Leveneur, Journal of CO2 Utilization.
3. RR **Jay** - Analytical chemistry, 1964

Acknowledgements

This study was carried out within the MICS (Made in Italy–Circular and Sustainable) Extended Partnership and received funding from the European Union Next-Generation EU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) – MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.3 –D.D. 1551.11-10-2022, PE00000004). Economic support from Åbo Akademi University Graduate School (Federica Orabona) is gratefully acknowledged.

Promoting zirconia with carbon: enhanced hybrid ZrO_2/C ketonization catalyst for the valorization of e-acetic acid

Jacopo DE MARON*[,1], Gaetano Maria D'ONOFRIO[1], Eleonora TOSI BRANDI[1], Andrea FASOLINI[1], Gloria GOTTARDI[2], Francesco BASILE[1], Fabrizio CAVANI[1], Tommaso TABANELLI[1].

[1]*University of Bologna, "Toso Montanari" Industrial Chemistry Dept., Viale Risorgimento 4, Bologna, Italy.*

[2] *Bruno Kessler Foundation, Center for Sustainable Energy., Via Sommarive 18, Trento, Italy.*

** Jacopo.demaron2@unibo.it*

Significance and Relevance

A novel hybrid catalyst was developed by deposition of ZrO_2 over a high surface area activated carbon. The material was investigated for the gas-phase ketonization of acetic acid (AA, 15wt.% aqueous solution) and thoroughly characterized to uncover structure-activity relationships. The carbon support created a hydrophobic environment at the boundary with ZrO_2 nanoparticles, hindering water adsorption on the active phase and preventing deactivation. The comparison with literature showed that the AC productivity in optimized conditions is among the highest reported so far, paving the way for the application to the valorization of AA derived from CO_2-electroreduction and fermentation.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion, CO_2 utilization and recycling
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Power-to-liquid (PtL) technologies aim at achieving a carbon-neutral energy cycle by converting CO_2 emissions into useful products. The electroreduction of CO_2 fuelled by renewable electricity (CO_2ER) can be exploited to produce valuable compounds such as acetic acid (AA) with satisfying faradaic efficiencies (e.g., Cu:Mg:Al-LDH-2:1:1/carbon paper, productivity = 2 $mmol_{AA}/h*g_{cat}$, FA = 84 %, voltage = -0.4 V vs RHE)[1] and even free from electrolytes and in relatively high concentrations with solid-state electrolyte membrane-electrode assemblies[2]. However, the production of longer-chain compounds with electrochemical methods remains extremely difficult. Instead, CO_2-derived AA could be used as a building block to produce multicarbon e-fuels and e-chemicals by means of well-established heterogeneous thermocatalytic processes such as ketonization, aldol condensation, aromatization, and hydrodeoxygenation. As previously mentioned, the AA produced by CO_2ER is diluted in water, which exerts a strong inhibitory effect on the activity of most ketonization and aldol condensation catalysts[3]. This issue is quite general and is encountered also when these processes are applied to other renewable feedstocks such as the water streams co-produced by the hydrothermal liquefaction of biomass or the volatile fatty acids produced by fermentation. Therefore, addressing the problem of mitigating water inhibition in the ketonization of both CO_2-derived and biomass-derived feedstocks is of paramount relevance.

Materials and Methods

Catalytic runs were carried out in a gas-phase plant operating at atmospheric pressure over 0.5 cm^3 of catalyst pellets (30-60 mesh). AA and water were mixed in the desired molar ratio and fed with a volumetric pump into a stainless-steel line to be vaporized before the catalytic bed. The LHSV and the flow of N_2 carrier were adjusted to obtain the desired molar fractions in the gas-phase maintaining a contact time t (at reaction temperature) = 0.5 seconds. The effluent from the reactor was condensed in a methanol-filled cold trap kept at 0 °C and analyzed offline with a Shimadzu GC 2010 PRO instrument quipped with FID detector (internal standard = dodecane, capillary column: HP-5, 30 m × 320 µm × 0.25 µm). The effluent from the cold trap was analyzed online by means of a Agilent 3000A micro GG equipped with a TCD detector (columns: PlotQ, OV1 and molecular sieve 5A).

ZrO_2 (62 m^2/g) and TiO_2 (149 m^2/g) benchmark materials were prepared by means of precipitation[4] and inverse microemulsion[5] respectively according to literature methods. 30 wt. % ZrO_2/C (488 m^2/g) was prepared by incipient wetness impregnation of a commercial Norit SX2 activated carbon with a Zr(IV)butoxide solution in butanol. The activated carbon was dried under vacuum at 100 °C before impregnation and the resulting wet solid was left 48 hours to hydrolyze with atmospheric moisture

before thermal treatment under N_2 up to 550 °C for 3 hours. Catalytic materials were characterized by means of N_2-porosimetry, XRD, XPS, TEM, SEM-EDS, Raman, and TGA.

Results and Discussion

The superior water-resistance of 30 wt. % ZrO_2/C was demonstrated by comparing its activity with that of ZrO_2 and TiO_2 in catalytic runs carried out at 350 °C, t = 0.5 s and feeding 50 wt. % AA aqueous solutions. Bulk ZrO_2 displayed commendable activity and selectivity in dry conditions but suffered from a severe lack of resistance in the presence of steam, resulting in the complete suppression of ketonization activity. On the other hand, TiO_2 exhibited a much higher water tolerance, retaining high activity with the steam-containing feed, but fell short in terms of selectivity due to coke formation (confirmed by low carbon balance, Raman and TGA), which occurred more extensively with the dry feed. Finally, the promotion of ZrO_2 with carbon enabled a much more selective ketonization of AA to AC both in dry condition and in the presence of steam, thus outperforming both bulk oxide benchmarks. Moving from these results, the concentration of AA in the feed was progressively reduced to 15 wt. %, and a complete conversion of AA with > 90 % selectivity to acetone was achieved at 400 °C. Reaction conditions were then further optimized achieving an acetone space-time yield among the highest reported so far in the literature for ketonization processes in the presence of steam (Figure 1A).

This work is significant because it demonstrates that the diluted AA in the aqueous stream at the outlet of state-of-the-art electrochemical CO_2ER flow-cells with solid-state electrolytes can be quantitatively converted into acetone with selectivities exceeding 90 % and STY > 3.5 h^{-1}. The same catalytic system could, in theory, have a wider application (e.g., ketonization of volatile fatty acid solution from fermentation, ketonization of the oxygenated molecules in aqueous streams co-produced by hydrothermal liquefaction etc.).

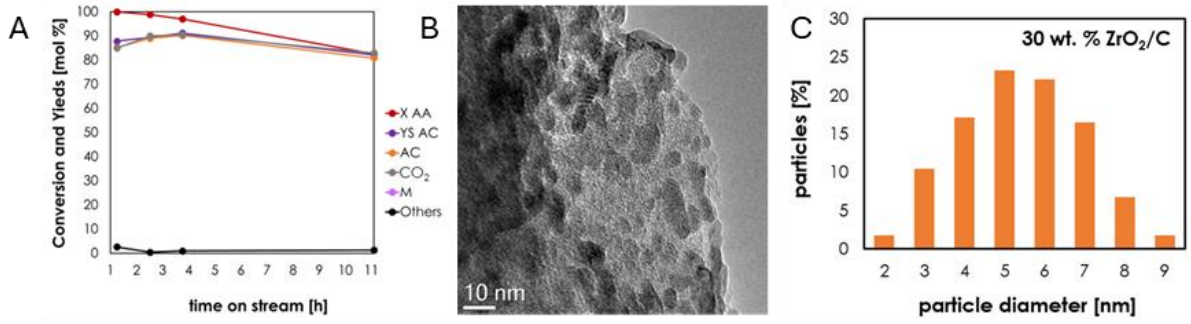


Figure 1 A: ketonization of 15 wt. % AA solution (0.25 cm^3 of 30 wt. % ZrO_2/C, T = 425 °C, τ = 0.125 s, 3 mol % of AA in gas-phase); B: TEM image of 30 wt. % ZrO_2/C; C: ZrO_2 particle size distribution.

References

1. M. Serafini *et al.*, *Advanced Functional Materials* **2023**, *33*, 2300345.
2. H-L. Zhu *et al.*, *Journal of the American Chemical Society* **2024**, *146*, 1144.
3. E.V. Fufachev *et al.*, *ACS Sustainable Chemistry & Engineering* **2020**, *8*, 11292.
4. J. De Maron *et al.*, *Sustainable Chemistry* **2021**, *3*, 58.
5. V. Maslova *et al.*, *Catalysis Today* **2021**, *380*, 147.

Acknowledgements

FB, JDM, TT and GG acknowledge the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3 - Call for tender No. 1561 of 11.10.2022 of Ministero dell'Università e della Ricerca (MUR); funded by the European Union – NextGenerationEU, PE0000021, "Network 4 Energy Sustainable Transition – NEST".

The contribution has been realized by a researcher (Andrea Fasolini) with a research contract co-financed by the European Union - PON Ricerca e Innovazione 2014–2020, 739 art. 24, comma 3, lett. a), della Legge 30 Dicembre 2010, n. 240 e s.m.i. e del D.M. 10 740 Agosto 2021 n. 1062.

Bifunctional catalysts for sorption-enhanced reaction processes

J.A.Z. PIETERSE*, G.D. ELZINGA, S. BOONEVELD, V. DIKIC
TNO Sustainable technology for industrial processes, 1755 LE Petten, Netherlands
** jean-pierre.pieterse@tno.nl*

Significance and Relevance

Sorption-enhanced reaction processes integrate adsorption capacity with catalytic reactions to directly convert reactants such as CO_2, methanol, and dimethyl ether into value-added fuels and chemicals within a single reactor, operating under relatively mild conditions and achieving high conversion. Material approaches to fully integrate the sorption and reaction functionalities avoid the challenging (e.g. abrasion, mass transfer) physically mixing of sorbents and catalyst particles.

Introduction and Motivations

The conversion of carbon dioxide (CO_2) to transport fuels with hydrogen has the potential of the integration of CO_2 capture and energy storage and conversion[1]. In particular, synthetic aviation fuel (SAF) production with renewable H_2 and CO_2 is attractive. Where in other transport direct electrification is feasible, hydrocarbons will remain the dominant fuel for airplanes. This drop-in fuel can be synthesized via the well-known Fischer-Tropsch route and via the emerging methanol route. Both synthetic routes benefit from a syngas containing CO and H_2, produced via the selective CO_2 reduction process to CO. The traditional thermochemical conversion is achieved by an endothermic reverse water-gas-shift reaction limited by thermodynamic equilibrium with low single pass conversion of CO_2 that operates above 850°C, requiring high energy input, creating a risk of catalyst deactivation and the formation of undesired side-products. The key challenge is to design a low temperature process that combines a high conversion with a high selectivity. The conversion at lower temperatures, i.e. 300 - 400 °C can be greatly enhanced if reaction product water is selectively removed[2]. Recently, first proof-of-concept was presented of the successful design of a bifunctional catalyst (reactive sorbent) for sorption-enhanced reverse water-gas shift (SE-RWGS, here designated as 'COMAX'), which combines CO_2 activation and water adsorption functionalities in an integrated reactive sorbent[3,4]. Here, we present COMAX optimization with reactive sorbent with focus on productivity, selectivity and cyclic stability. This contribution also highlights our advances in the integration of functionalities with other sorption-enhanced reaction processes. An outlook to the utilization of these materials in pressure swing adsorption cycle design and process integration will also be presented. The successful integration of catalytic activity and adsorption capacity into a single particle opens opportunities in the further intensification of sorption-enhanced reactions.

Materials and Methods

Experimental runs up to 30 bar(a) pressure were conducted on two high-pressure test rigs. During adsorption, the reactor was operated between 250 and 1200 h^{-1} at temperatures up to 400 °C. The gas mixtures consisted of various CO_2:H_2 ratios and 5 mol% argon as tracer. Reactive sorbent regeneration consisted of periodic switching to dry nitrogen, feed or product gas followed by decreasing the pressure to 1 - 3 bar(a). Gas analysis was performed by a gas chromatograph (uGC, equipped with TCD and FID), non-dispersive IR analyzer (NDIR) and a mass spectrometer (MS). Molecular sieve beads 4A zeolite (2-3 mm) were used with incipient wetness impregnation with $H_2PtCL_6.6H_2O$ to obtain the reactive sorbent with Pt loading of 0.3wt%.

Results and Discussion

Figure 1 gives an example of the reactive adsorption step that typically convert over 90% of CO_2 to CO by the simultaneous RWGS reaction and adsorption of the product water. The selectivity of the process is governed by the time, i.e. the step time chosen for adsorption in the (pressure swing adsorption) cycle. Table 1 gives an example of the typical product distribution that can be obtained.

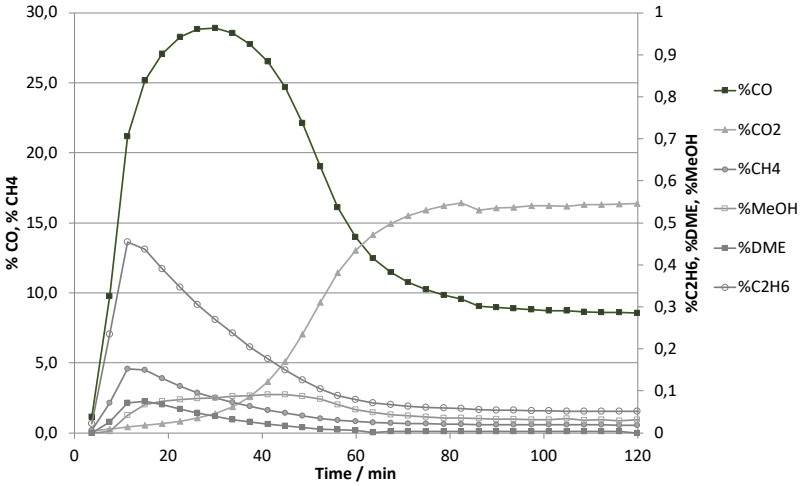


Figure 1. Example of the reactive adsorption step on 0.3wt%Pt_4A molecular sieve using 69,3% H_2, 25,7% CO_2, 5,0% Ar tracer at 390 °C, 25 bara, ±280 h^{-1}, 80 sccm.

Table 1. Product distribution based on 40 min. productivity using 71,3% H_2, 23,8% CO_2, 5,0% Ar tracer at 370 °C, 25 bara, ±280 h^{-1}, 80 sccm.

	CO (%)	**CO_2 (%)**	**CH_4(%)**	**DME(%)**	**MeOH(%)**	**C_2H_6(%)**
0.3wt%Pt_4A	87,5	6,7	4,6	0,4	0,4	0,4

0.3wt%Pt_4A was also tested in full pressure swing cyclic mode with (reactive) adsorption, blowdown, purge and repressurization steps and revealed very good cyclic stability provided that the temperature during the regeneration steps was high enough to ensure near-complete dehydration (>350 °C).

References

1. K.M.K. Yu, I. Curcic, J. Gabriel, S.C.E. Tsang ChemSusChem **2008**, 1, 893.
2. B.T. Carvill, J.R. Hufton, M. Anand, S. Sircar, American Institute of Chemical Engineers Journal **1996**, 42, 2765.
3. J.A.Z. Pieterse, G.D Elzinga, S. Booneveld, J. van. Kampen, J. Boon, Catalysis Letters **2021**, 152, 460.
4. J.A.Z. Pieterse, G.D. Elzinga, WO2021240017A1, **2021.**

Acknowledgements

Dr. Andreas Geisbauer is gratefully acknowledged for providing the molecular sieve and reviewing.

Mechanistic Link to Electrode Magnetism in Magneto-Electrocatalytic Oxygen Evolution

Amy Radford[1], Dorottya Szalay[1], Chen Wu[2], Yiyang Li[1*], Edman Tsang[1]
[1]*Wolfson Catalysis Centre, University of Oxford, Oxford, England*
[2]*School of Materials Science and Engineering, Zhejiang University, Hangzhou, China*
*yiyang.li@chem.ox.ac.uk

Significance and Relevance

Controlling electrocatalytic water-splitting with magnetic fields (MFs) could offer a simple approach to unlocking higher performance in industrial electrolysis. This work presents novel results for ferromagnetic Ni and paramagnetic Pt as working electrodes in magneto-electrocatalytic oxygen evolution. By investigating the catalytic performance at various MF strengths and orientations, a qualitative assessment is made of the governing magneto-electric mechanisms in these systems. A model of a thorough experimental approach for proper analysis of magnetic effects is demonstrated.

Preferred and 2nd choice for the topic: Sustainable and clean energy production and transport / Advanced process with electrocatalysis and plasma utilization

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Magneto-electrocatalytic water-splitting has been widely researched but is not yet well understood due to the complicated nature of magneto-electric (ME) mechanisms. These mechanisms tend to originate from Lorentz force, Kelvin force, and electrode spin-polarization; they present as magnetohydrodynamics (mass transport), magnetoresistance (charge transport), and promoted $^3O_2$ formation.[1] The reported ME effects on performance vary wildly, with some systems demonstrating enhancements of up to 650% and some succumbing to negative effects.[2,3] The large disparity between reports can be attributed to interference of ME mechanisms, where the dominant mechanism heavily depends on factors such as: electrode composition, relative MF orientation, and MF strength.

Materials and Methods

Electrochemical measurements were performed using a 3-electrode system with a Hg/HgO reference electrode and Pt sheet (1x1 cm^2) counter electrode in 1M KOH electrolyte. For the working electrode (1x1 cm^2), Ni foam, Ni sheet, and Pt sheet were compared. Using a CHI640E Potentiostat, chronoamperometry measurements were performed and magnetic effects were calculated from changes in current density. MFs up to 800 mT were imposed using an electromagnet.

Results and Discussion

Ni is a strong ferromagnet and Pt is a weak paramagnet; this comparison facilitates understanding of how spin polarization and local magnetic flux density link to the domination of certain ME mechanisms. Initial studies (Fig. 1A) show a positive correlation between effect magnitude and MF strength, particularly for Ni foam and Pt sheet. The MF enhances Ni performance and worsens Pt performance. It could be assumed from this result that, for Ni, the strong magnetic flux density and greater spin-alignment favors ME mechanisms such as: Kelvin force attracting reactive radicals in the electrolyte, magnetohydrodynamics shortening the diffusion layer, and promoted formation of paramagnetic $^3O_2$. The Pt, on the other hand, should have a weak affinity to these enhancement mechanisms and so may have succumbed to increased charge-carrier resistance within the electrode, known as positive magnetoresistance.

To investigate further, the magnetic effects were studied for each system in four orientations (Fig. 1B & 1C): 0° (original), 90°, 180°, 270°. Considering the Ni electrodes first, the strong dependence on

orientation which leads to a negative effect at 180° and 270° suggests that Kelvin force and favored $^3O_2$ formation are not dominant mechanisms. The orientation-dependent Lorentz force, therefore, is the likely origin of dominant ME mechanisms – magnetohydrodynamics and intra-electrode charge-carrier movement – in the Ni systems. The persistent negative effect exhibited by the Pt supports the hypothesis of positive magnetoresistance dominating this system.

The optimal conditions demonstrated in this work (ferromagnet, 90°) should be considered in future studies pushing similar systems towards industrialization.

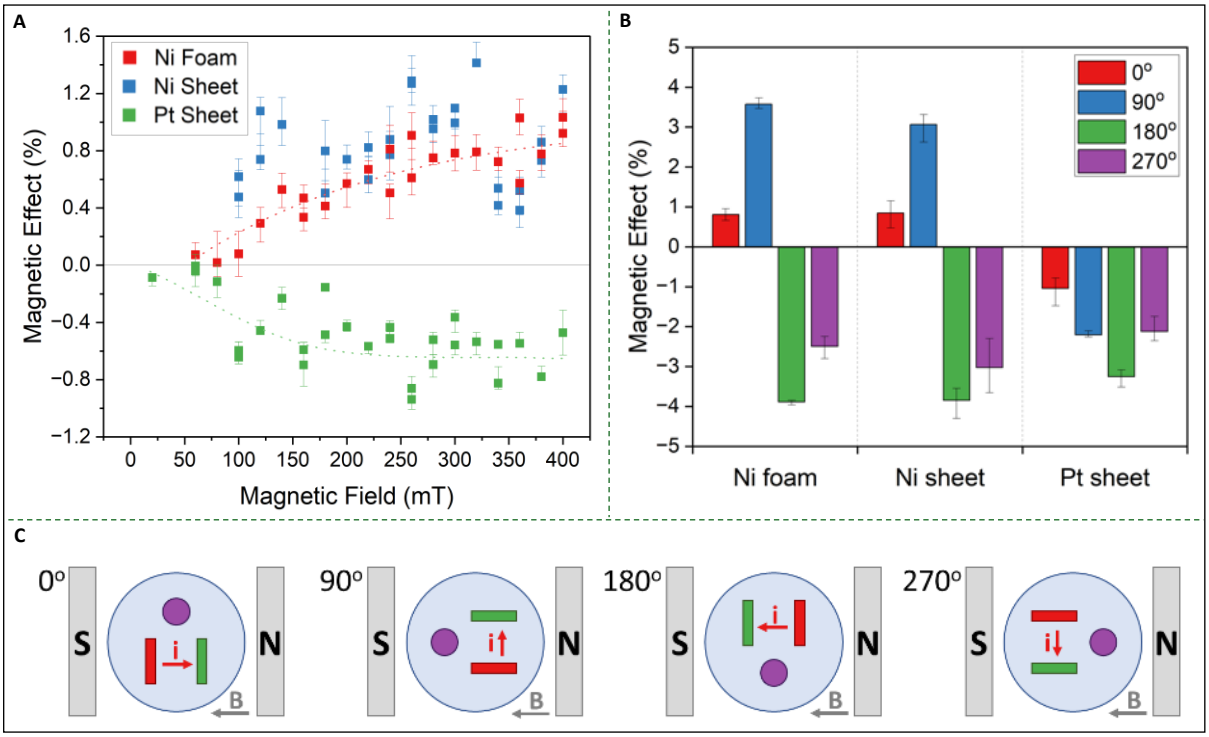


Figure 1. [A] Plots of magnetic effect vs MF strength in 0°-orientation for each working electrode. Magnetic field was ramped in 20 mT intervals from 0 to 400 mT. [B] Graph showing magnetic effect at 800 mT for four orientations for each working electrode. [C] Schematic showing a top-down view of the electrocatalytic setup in the four orientations relative to the MF, B. The red, green, and purple shapes represent the working, counter, and reference electrodes, respectively.

References

1. S Luo, K. Elouarzaki, Z. Xu, *Angew. Chem.* **2022**, *61*, e202203564
2. J. Saha, R. Ball and C. Subramaniam, *ACS Sustain. Chem. Eng.*, **2021**, *9, 7792–7802*
3. M. Lin, L. Hourng, C. Kuo, *Int. J. Hydrogen Energy*. **2012**, *37,* 2

Development of an innovative biorefinery process by the one-pot fractionation of defatted cardoon

Sara FULIGNATI[*,1], Francesca BARSOTTI[1], Nicola DI FIDIO[1], Domenico LICURSI[1], Stefano FRIGO[2], Claudia ANTONETTI[1], Anna Maria RASPOLLI GALLETTI[1]
[1]*University of Pisa, Department of Chemistry and Industrial Chemistry, via G. Moruzzi 13, Pisa, Italy.*
[2]*University of Pisa, Department of Energy, System, Territory and Construction Engineering (DESTEC), Largo L. Lazzarino 1, Pisa, Italy.*
**sara.fulignati@unipi.it*

Significance and Relevance

The one-pot fractionation of defatted cardoon through biphasic organosolv process was conducted under the efficient microwave heating that allowed the separation and recovery of each biomass fraction. Subsequently, these fractions were characterized and valorized according to the Green Chemistry principles to provide high-quality lignin, to be employed as an antioxidant and in materials formulation, furfural, which is a relevant platform chemical and butyl levulinate, which can be advantageously adopted as bio-blendstock in mixture with Diesel or gasoline. Thus, for the first time, the complete exploitation of the waste defatted cardoon was successfully performed, contributing to developing the biorefinery process.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion; Sustainable and clean energy production and transport.
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Since 2020 the European Union, by subscription of the Green Deal, fixed the aim of carbon neutrality by 2050. For this purpose, it is fundamental to reduce the net carbon emissions, and one possible strategy is the replacement of fossil resources with renewable ones.[1] Under this perspective, lignocellulosic biomass represents a valid renewable resource because it can be converted into a plethora of valuable chemicals and fuels. Among the biomasses, cardoon is an interesting feedstock being a perennial herbaceous crop that can grow on marginal lands. Up to now, the seeds of the cardoon flower have found applications for bio-diesel production, whilst the cardoon residues (defatted cardoon) are generally pretreated by the steam explosion, which is mainly focused on cellulose exploitation leading to hemicellulose degradation and recovery of low-quality lignin.[2] However, from the perspective of a biorefinery scheme, all the biomass fractions should be valorized, thus minimizing the waste. On this basis, the present work investigated the one-pot fractionation of defatted cardoon through the biphasic (*n*-butanol/water) organosolv process to recover and valorize each biomass fraction. Then, to effectively develop a biorefinery process, the recovery and characterization of lignin, and the conversion of hemicellulose and cellulose to furfural and butyl levulinate, respectively, were performed. Noteworthy, the *n*-butanol adopted for the butanolysis of cellulose was recovered by the lignin separation step, thus reducing the total amount of employed solvent according to the Green Chemistry principles. Lastly, also the solid by-product (char) deriving from the butanolysis step was characterized to propose its possible applications, thus effectively valorizing all the products of the proposed process.

Materials and Methods

The organosolv process was performed adopting the biphasic system *n*-butanol/water acidified with diluted H_2SO_4 under microwave heating with the monomodal reactor CEM Discover S-class System. Thus, at the end of the pretreatment, lignin was solubilized in the organic phase, hemicellulose was depolymerized to give mainly xylose that was recovered in the aqueous phase, and cellulose was recovered within the solid residue (cellulose-enriched residue). Lignin was then isolated by vacuum removal of the solvent and its quality was evaluated by optical microscopy, FT-IR and elemental

analysis characterizations. Xylose present in the aqueous phase was directly converted to furfural under microwave heating employing H_2SO_4 as catalyst. The chemical compositions of defatted cardoon and cellulose-enriched residue were determined by the NREL procedure[3] to evaluate the effective removal of lignin and hemicellulose. The cellulose-enriched residue was then converted to butyl levulinate under microwave heating employing H_2SO_4 as catalyst and as solvent/reactant *n*-butanol recovered by the lignin separation step. Finally, the solid char deriving from the butanolysis step was characterized by FT-IR and elemental analysis techniques.

Results and Discussion

The organosolv process was investigated studying the influence of temperature and acid loading on lignin and hemicellulose removal The increase of both temperature and acid loading positively affected the effectiveness of the pretreatment leading to the highest lignin and hemicellulose removals of 72 and 97 wt%, respectively, and to the contemporary enrichment of cellulose within the solid residue, which reached 74 wt%. Moreover, these conditions promoted hemicellulose depolymerization leading to an aqueous phase enriched in xylose that was quickly converted to furfural up to a yield of 52 mol%. The optimization of cellulose-enriched solid residue butanolysis was optimized reaching the highest yield of 46 mol%, higher than that reached starting from not pretreated defatted cardoon (36 mol%), thus proving the effectiveness of the organosolv approach. A char yield of 6 wt% was ascertained under the optimized butanolysis conditions and the characterization of this by-product highlighted a promising higher heating value that made it a potential solid fuel. To prove the effectiveness of butyl levulinate as bio-blendstock, it was added as bio-blendstock to Diesel/gasoline and tested in real engines, leading to a decrease of polluting emissions without affecting the engine performance. Last but not least, very pure lignin was recovered from the organic phase, as proven by FT-IR and elemental analysis characterizations.

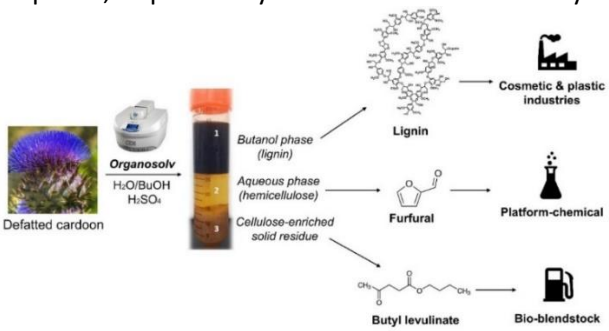


Figure 1. Scheme of the developed biorefinery scheme.

In conclusion, the complete exploitation of all the defatted cardoon fractions to give a valuable bio-fuel, a platform chemical, and lignin, employable as an antioxidant and in materials formulation, was successfully performed.

References

1. L. Chen, G. Msigwa, M. Yang, A.I. Osman, S. Fawzy, D.W. Rooney, P.S. Yap, *Env. Chem. Lett.* **2022,** *20,* 2277-2310.
2. A.M. Raspolli Galletti, D. Licursi, S. Ciorba, N. Di Fidio, V. Coccia, F. Cotana, C. Antonetti, *Catalysts* **2021**, *11*, 1082.
3. A.M. Raspolli Galletti, R. Lorè, D. Licursi, N. Di Fidio, C. Antonetti, S. Fulignati, *Catal. Today* **2023**, *418*, 114054.

Acknowledgements

The authors are grateful to the European Union and Italian Ministero dell'Università e della Ricerca for the financial support provided through the PNRR project NEST. Project code PE0000021, Concession Decree No. 1561 of 11.10.2022 adopted by Ministero dell'Università e della Ricerca (MUR), (CUP I53C22001450006) Spoke n. 3 BIOENERGY & NEW BIOFUELS FOR SUSTAINABLE FUTURE.

Temperature mapping of fixed-bed reactor in microwave-assisted catalytic dry-reforming of methane over SiC-based catalysts

Andrea MERLO, Léon THOMANN, Nolven GUILHAUME*, Yves SCHUURMAN
IRCELYON, UMR5256 CNRS and University Claude Bernard Lyon 1, Villeurbanne, France
**nolven.guilhaume@ircelyon.univ-lyon1.fr*

Significance and Relevance

Ni/SiC catalysts can be rapidly and efficiently heated at high temperature under microwaves. The catalysts exhibit good performances for the DR of methane. However, the specificity of microwave heating can lead to large temperature gradients in a fixed-bed reactor. This work shows that catalyst shaping is very important to obtain uniform heating of the catalytic bed.

Preferred topic: Catalysis to electrify the chemical production; 2nd choice topic: green H_2 production
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Catalytic dry reforming (DR) of methane allows converting two greenhouse gases (CH_4 and CO_2) into syngas (H_2 + CO), which is a potential source of methanol, synthetic hydrocarbons and hydrogen. The reaction is highly endothermic and requires high temperatures, while catalyst deactivation due to coking and sintering can be an important issue that limits its industrial applications. The use of microwave (MW) heating could help overcome part of these limitations by providing a new and more energy-efficient way to heat the solid catalyst directly, avoiding heat transfer limitations[1].
In this study, an innovative reactor using MW heating and a MW-susceptible DR catalyst have been developed.

Materials and Methods

A porous SiC under the form of powder (100-200 mm) or pellets (2x2 mm) was impregnated with nickel nitrate and calcined in air to obtain a Ni loading of 5 wt.%. The catalyst was reduced under H_2 at 650°C before the catalytic tests. Microwave-assisted catalysis was carried out in a tubular quartz reactor housed in the cavity of a single mode MW generator (SAIREM GMP G3, 2 kW) operating at 2.45 GHz, equipped with an optical pyrometer for temperature control and an IR camera for temperature mapping of the catalytic bed. The DR reaction was carried out between 700 and 900°C with a mixture of CO_2:CH_4:(N_2+He) of composition 0.6:0.2:0.2. Quantitative online gas analysis of gases (CH_4, CO, CO_2, H_2, light HCs) was performed with a micro-GC using He as internal standard.

Results and Discussion

The most challenging task during MW heating of a solid catalyst is the catalyst temperature control. It is not possible, as with an electric furnace, to place metallic thermocouples along the catalyst bed since metals deflect the electromagnetic field and can cause arcing. Achieving a homogeneous absorption of MW along the catalyst bed is difficult, especially since the reaction is highly endothermic, which can lead to temperature gradients while the microwave absorption properties of the material also vary with temperature.

Fig. 1 compares the temperature profiles recorded in the catalyst bed under the same MW power, for the Ni/SiC catalysts under powder or pellets form. The Ni/SiC powder displays a homogeneous temperature profile along the catalyst bed, whereas the Ni/SiC pellets bed shows an uneven temperature within the pellets and large temperature gradients between the core and the surface of the pellets, as well as at the contact points between the pellets.

Fig. 2 shows the effect of catalyst shaping on the performances for dry reforming of methane, at the same temperature of 750°C controlled and regulated on the basis of the pyrometer temperature reading. Clearly, the performances of the Ni/SiC pellets catalyst are impaired by the poor and uneven

temperature distribution and the presence of some very hot spots does not compensate for the drop of catalytic activity at the colder spots.

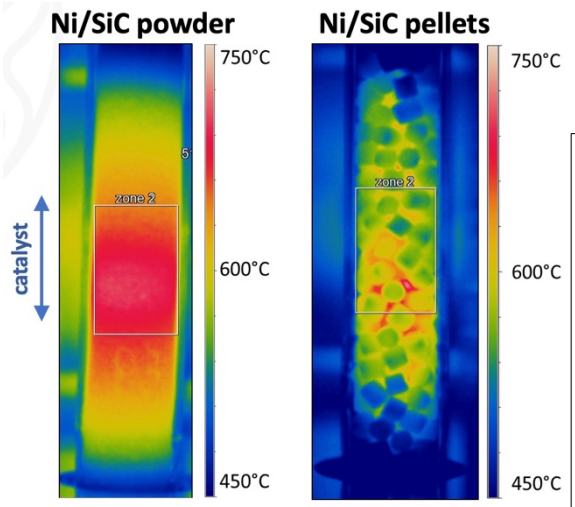


Figure 1. Temperature profiles in the catalyst bed recorded with the IR camera

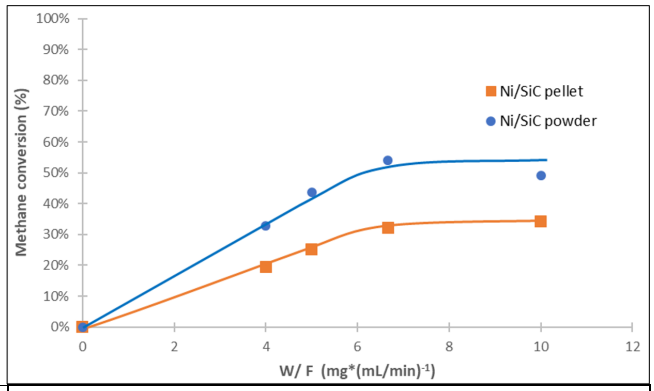


Figure 2. Performance of Ni/SiC powder and pellets catalysts for DR of CH_4 at 750°C (pyrometer reading) as a function of W/F.

Conclusion

Microwaves can efficiently and rapidly heat suitable catalysts to the high temperatures required for DR of methane. However, the catalyst shaping must be adapted to this specific heating method, notably in the perspective of industrial applications, and the catalyst bed temperature must be carefully controlled.

References

1. S. Horikoshi, N. Serpone, Catal. Sci. Technol. **2014**, 4, 1197.

Acknowledgements

The authors gratefully acknowledge the funding of the European Commission (eQATOR project, Grant agreement n° 101058293).

Zn-based catalyst route for Pentaerythritol synthesis: Process related CO_2 reduction

Aqsa NOREEN.[1] Derek CREASER.[1], Oleg PAJALIC.[2], Louise OLSSON*[1]
[1] *Competence Center for Catalysis, Chemical Engineering, Chalmers University of Technology, SE-422096 Gothenburg, Sweden*
[2] *Perstorp AB, Industriparken, 284 80 Perstorp, Sweden*
**louise.olsson@chalmers.se*

Significance and Relevance

To date industrially production of penta has relied on a homogeneous catalysis process that requires numerous post-separation steps to achieve high purity. This approach is energy intensive and results in significant CO_2 emissions. However, there are no published papers where a heterogeneous catalyst has been used for penta synthesis. We have therefore, for the first time, developed a novel heterogeneous catalysis route to form penta from aldehydes by using a Zn-based catalyst. This is an attractive alternative for producing penta with less solvent and simpler separation steps as shown in Figure 1(b).

Preferred and 2nd choice for the topic: Preferred "Catalysis to electrify the chemical production" and 2nd choice "Green chemistry and biomass transformation, renewable resources conversion"
Preferred presentation: *(Oral preferred/Short Oral preferred. If not selected, then can go for Poster.*

Introduction and Motivations

Pentaerythritol (Penta) is a common platform chemical used in the production of resins, plastics, paints, and various other commercial products [1]. Industrially, penta is produced with high over-all yields and a good product grade through a homogeneous catalysis system in which formaldehyde and acetaldehyde undergo three sequential cross condensation reactions followed by the cannizzaro reaction in the presence of a liquid alkaline solution. In this existing liquid alkaline homogeneous catalysis system, an excess of formaldehyde and alkaline solution is needed due to the formation of sodium formate salt as a byproduct during the reaction [2]. As an alternative, a heterogeneous catalytic system is introduced in this work, in which a solid catalyst can make the process less complicated by reducing the amount of water solvent and replacing the alkaline solution. Moreover, this can also decrease formaldehyde usage which can potentially reduce CO_2 emissions, since formaldehyde synthesis produces process related CO_2.

For this purpose, Zn based non-alkaline catalysts were prepared and tested for the synthesis of penta. There are several studies which explain the potential of Zn-based catalysts for many hydrogenation and aldol reactions [3]. However, there is limited literature that explains the bifunctionality of Zn based catalysts to initiate aldol and cannizzaro reactions simultaneously. It is found in this study that Zn based catalysts such as ZnO and Zn over different supports prepared through different methods have different catalytic activity towards aldol condensation products and for penta synthesis.

Materials and Methods

Zn/SnO_2 (WI), Zn/Al_2O_3 (WI), and Zn/ZSM-5 (WI) were prepared by a conventional wet impregnation method, and Zn/ZSM-5(IE) was prepared by an ion exchange method. All the catalyst activity tests were performed in a 300 ml stainless steel batch reactor (Buchiglas). Formaldehyde and acetaldehyde were mixed with the solid catalysts and the reactor was flushed to contain N_2 at atmospheric pressure before heating up to 200 ^oC, while continuously stirred at 500 rpm for 2 h when the reaction temperature was reached. After cooling down the reaction mixture, the solid catalysts

were separated out from the liquid reaction mixtures. Products were then analyzed and quantified by GC/MS.

Results and Discussion

High surface area ZnO was used as catalyst, and it can be seen in the figure that it shows high activity towards penta formation as selectivity reached 46% with 100% conversion of formaldehyde. Among all the tested catalysts, MeOH was formed predominantly along with penta derivatives that mainly consisted of dipentaerythritol and cyclic monoformals of penta (CPF). Other by-products included mainly 2-butenal, acetic acid and 2-buten-1,4-diol named as (oxys+acids+diols) in the graph. Except the liquid product distribution shown in the graph by columns, gas products were also produced due to the cracking reactions reported as gas yield (C%) which accounted for 14-18% of the carbon contained in the feed reactants. Amongst the catalysts that were prepared by the WI method, Zn/SnO_2 showed the best performance for penta synthesis with less by-product formation. Moreover, catalyst Zn/ZSM-5 (IE) prepared by ion exchange showed the least activity towards penta formation which might be due to the poor activity of Zn ions for catalyzing the reaction. In control experiments without the catalysts there was undetectable yield of penta or its derivatives.

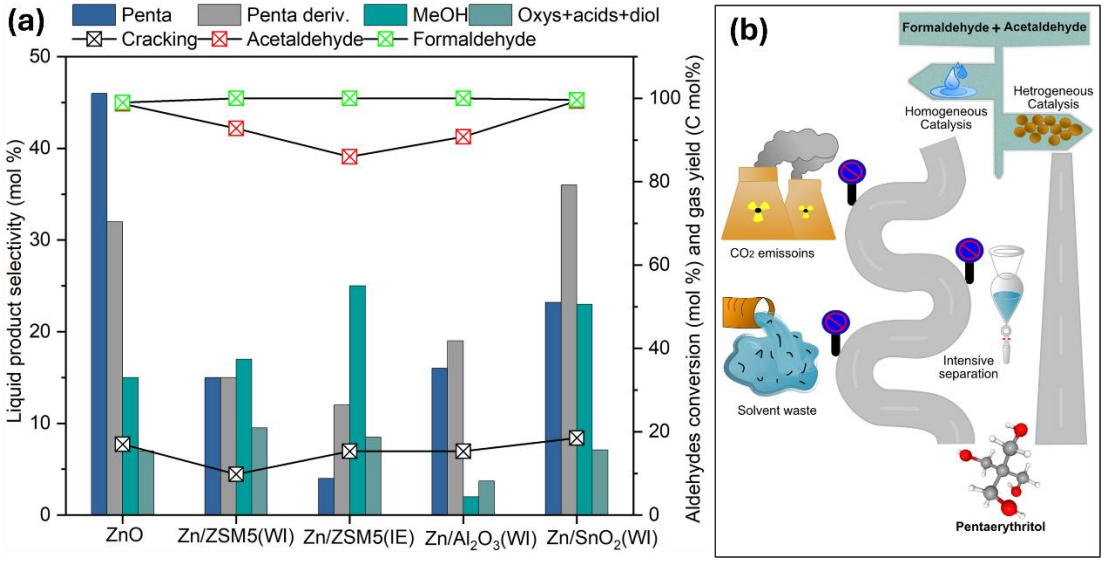


Figure 1. (a) Performance of Zn-based catalysts, Reaction conditions: formaldehyde: acetaldehyde 5:1 (mol:mol), formaldehyde 37 wt% in water, 200 °C, 0.5 g catalyst, 500 rpm, 2 h reaction time, **(b)** Schematic diagram of pentaerythritol synthesis by homogeneous and heterogeneous catalysis routes.

References

(1) Khademi, Z.; Nikoofar, K.; Shahriyari, F. Pentaerythritol: A Versatile Substrate in Organic Transformations, Centralization on the Reaction Medium. *Curr Org Synth* **2019**, *16* (1), 38-69.

(2) E., L. Process for the Preparation of Pentaerythritol, US005741956A. 1998.

(3) Chen, G.; Zhao, Y.; Shang, L. Recent Advances in the Synthesis, Characterization and Application of Zn+-containing Heterogeneous Catalysts. *Advanced Science* **2016**, *3* (7), 1500424.

Acknowledgements

This work is performed in Competence Center for Catalysis at Chalmers University of Technology in collaboration with Perstorp AB.

"Redox Behavior of Manganese Oxide Catalysts in Thermochemical Redox Cycles: Mechanistic Insights from In Situ TEM and DFT Investigations"

Joanna GRYBOŚ[1], Karol GÓRECKI, Monika FEDYNA, Michał PACIA, Zbigniew SOJKA
[1]Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Kraków, Polska.
** joanna.grybos@uj.edu.pl*

Significance and Relevance

Due to the complexity of thermochemical redox cycles (*cf.* Figure 1), and an important number of factors influencing their course, despite extensive research, a comprehensive and unambiguous interpretation of the role of redox changes in manganese oxide-based catalysts is still lacking. Scientific literature is lacking detailed mechanistic description of the temperature-induced reduction of manganese oxide catalysts ($K_2Mn_8O_{16}$ and $Na_2Mn_3O_7$) catalysts, the concomitant phase, structure, and morphology changes, sintering processes, mechanisms of surface and bulk oxygen migrations and release, and the mechanism of vacancies formation and migration. This research presents mechanistic insights into temperature-induced structural, morphological, and redox changes in manganese oxide catalysts within the context of thermochemical redox cycles. It provides an understanding of the role of different redox couples (Mn^{4+}/Mn^{3+} or Mn^{3+}/Mn^{2+}), comproportionation and disproportionation of manganese cations ($Mn^{2+}+Mn^{4+}\rightarrow 2Mn^{3+}$). This research can thus guide the implementation of specific manganese oxides in water and carbon dioxide splitting.

Preferred and 2nd choice for the topic: Fundamental advances in understanding catalysis, Sustainable and clean energy production and transport
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Two-step metal oxide thermochemical redox cycles have often been studied in the context of converting heat to chemical energy, which can be further used for energy storage, renewable fuel production, air separation, and oxygen pump. The development of these applications depends on the selection of appropriate redox materials, which must be optimized for each specific use. A wide range of scientific research indicates that oxides that preserve a complete phase transition during reduction possess significantly higher specific energy storage compared to materials, such as ceria and perovskites, that undergo partial reduction. On the other hand, partial reduction materials generally exhibit faster kinetics and greater activity at lower temperatures. Therefore, the selection of materials for different applications often involves a trade-off between the significance of high specific energy storage and the advantages of fast kinetics and operation at low temperatures. In this context, our objective is to provide comprehensive knowledge regarding the general mechanism and environmental factors governing thermochemical redox cycles on the exemplary materials i.e. manganese oxide-based catalysts. Two types of oxides were selected: those that undergo partial reduction ($K_2Mn_8O_{16}$ and $Na_2Mn_3O_7$). The research aims at explaining the effect of temperature on the redox behavior of the proposed manganese catalysts during the thermochemical redox cycles, including thermal activation of the catalysts, their phase, and structural stability, mechanisms of surface and bulk oxygen migration, and mechanism of vacancies formation and migration, which are all responsible for the catalyst's redox performance and are involved in the sintering processes as well.

Materials and Methods

The research was conducted by employing the complementary use of advanced microscopic (SEM, TEM, STEM, ED, EDX, EELS, including in-situ mode), and theoretical (ab initio DFT and atomistic thermodynamics calculations) methods. In addition, several basic characterization techniques were applied to gain insight into the phase and chemical composition of the materials (XRD, XRF) and to characterize the short-range order of their atomic structures (IR, Raman).

Results and Discussion

The examined manganese catalysts were prepared via hydrothermal and solid-state syntheses, using different precursors (manganese acetate, manganese sulphate, manganese nitrate) and reducing

agents (e.g. glucose). Subsequently, only those exhibiting well-defined morphologies were selected for further analysis. Ex-situ microscopic characterization of the catalysts revealed differences in the redox state of manganese ions depending on their position within the catalyst material. For the $K_2Mn_8O_{16}$ catalyst, the ELNES spectra analysis showed a chemical shift of the Mn energy loss to lower values, indicating changes in the Mn valency state from the core (Mn^{4+}) to the tip/surface (Mn^{2+}/Mn^{3+}). In-situ TEM and EELS experiments focused on thermally-induced redox changes demonstrated discrepancies in redox properties and stability between nanorods and layered manganese catalysts. The EELS analysis was complemented by DFT modeling, which provided insights into oxygen vacancies formation and their migration within the atomic structure of the $K_2Mn_8O_{16}$ and $Na_2Mn_3O_7$ catalysts. Through a combination of ex-situ and in-situ experiments with the DFT results, it was possible to identify a temperature window where both catalysts exhibited fully reversible redox behavior, as well as stable structure and morphology. This comprehensive approach contributes to a deeper understanding of the redox processes occurring in the manganese-oxide-based catalysts and their potential applications in thermochemical cycles.

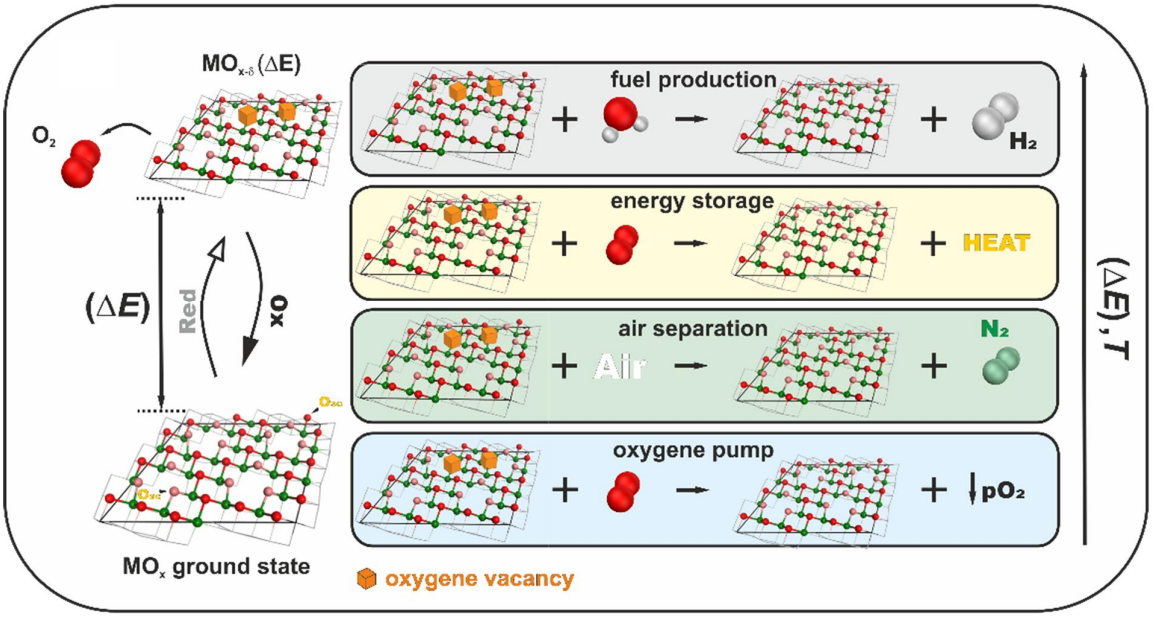


Figure 1 Schematic presentation of two-step thermochemical redox cycles, where the heat-produced chemical energy is applied for renewable fuel production, energy storage, air separation, and oxygen pump.[1]

[1] J.Mater. Chem. A, 2017, 5, 18951

Acknowledgements: The authors thank the Polish National Science Centre for funding (OPUS Grant Number 2023/49/B/ST4/00740).

Unraveling the catalytic activity of FeCo alloys for ammonia decomposition via molecular dynamic simulations

Simone PEREGO[1]*, Luigi BONATI[1], Michele PARRINELLO[1]
[1] *Istituto Italiano di Tecnologia, Atomistic Simulations, 16165 Genoa, Italy.*
* *simone.perego@iit.it*

Significance and Relevance

This study establishes a robust, data-efficient framework for simulating catalytic processes under realistic conditions. This allowed us to study for the first time ammonia decomposition on FeCo via molecular dynamic (MD) simulations, revealing its reaction mechanism on the atomistic scale. Our simulations provide a rational explanation of the promoter effect of alloying, laying the foundation for a knowledge-based design of sustainable catalysts for H_2 production from ammonia.

Preferred and 2nd choice for the topic: H2 storage and transportation, hydrogen vectors
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster) Oral preferred or Short Oral

Introduction and Motivations

Ammonia is considered a potential hydrogen vector due to its high hydrogen content and ease of transportation and storage. However, on-site carbon-free hydrogen production requires the development of efficient methods of hydrogen extraction from ammonia. To this end, iron-based catalysts are widely employed in the thermocatalytic cracking of ammonia. Despite more than a century of studies, the cracking reaction steps are still not well characterized due to the operative temperature conditions (700-800 K).[1] Several DFT-based theoretical studies have elucidated the process at T=0 K. However, the resulting reaction profiles do not reflect the operando conditions and do not consider the dynamic behavior of the surface catalyst. In fact, surface dynamics play a critical role in heterogenous catalysis, explaining activity and long-term stability.[2] Our recent studies on ammonia decomposition on Fe at the operando temperature via machine learning (ML) based MD reveal the complexity of this process and the non-trivial effects of finite temperature description. For the dehydrogenation steps, we found a unique reaction mechanism over an ensemble of reaction pathways[3]. Furthermore, in combination with experiments, we rationalized the early stage of Fe(110) nitridation under ammonia decomposition[4]. In this study, we focus on FeCo alloy, which has recently been proposed as an alternative to Fe as a catalyst for ammonia decomposition, given its superior activity and stability[5]. Catalytic cracking of NH_3 on FeCo has never been studied at the atomistic level, even with static methods, given the combination of complexity and high computational cost. To do so, we developed a new protocol to construct potential MLs in a data-efficient manner, in addition to the use of advanced dynamics simulations. This allowed us to study the complete reaction at operating temperatures at a fraction of the cost, revealing the microscopic origin of the promoter effect of alloying iron with cobalt.

Materials and Methods

To build our interatomic ML-potential we employed a two-stage protocol to achieve data efficiency while delivering high accuracy along the reaction pathways. In the exploratory phase, uncertainty-aware flooding simulations were conducted using Gaussian Processes (GPs) to identify reactive configurations. Enhanced sampling techniques, such as On-the-Fly Probability Enhanced Sampling (OPES), facilitated the efficient exploration of transition states and metastable configurations under high-temperature conditions. The convergence phase utilized equivariant graph neural networks (GNNs) to consolidate the dataset and provide a uniformly accurate potential. A novel Data-Efficient Active Learning (DEAL) algorithm was developed to refine the training dataset further. DEAL integrates query-by-committee uncertainty estimates from GNNs with the assessment of local environment similarity via GPs to systematically select a subset of relevant configurations to be recalculated at the DFT level. This ensures accurate modeling of the potential energy surface with minimal demand for QM calculations.

Results and Discussion

Our workflow required approximately 1,000 DFT calculations per reaction step; a reduction of more than 20-fold compared to previous studies[3,4,6,7]. The DEAL approach systematically identified non-redundant configurations, ensuring uniform accuracy along reactive pathways while limiting the training set size.

Enhanced sampling simulations revealed complex, multi-channel reaction mechanisms for ammonia dehydrogenation, including $NH_3 \rightarrow NH_2 + H$, $NH_2 \rightarrow NH + H$, and $NH \rightarrow N + H$ steps. Free energy profiles were reconstructed with a sampling error of less than 20 meV, revealing an ensemble of transition states and reaction pathways for each with similar barriers but distinct geometric configurations. These simulations captured the dynamic evolution of FeCo active sites under operando conditions, offering microscopic insights into surface-catalyzed reactions.

More importantly, the ML-based simulations revealed the microscopic origin of the higher catalytic activity of the alloy with respect to the pure Fe catalyst, which is both a lowering in the activation energy of the rate-limiting step (nitrogen recombination) and a higher resistance to nitridation (Fig 1). The latter is originated from a combination of multiple aspects, revealing the necessity of a full dynamic description. The theoretical results were validated by experimental evidence of no bulk nitride formations in FeCo during ammonia decomposition, contrary to what was observed for Fe.

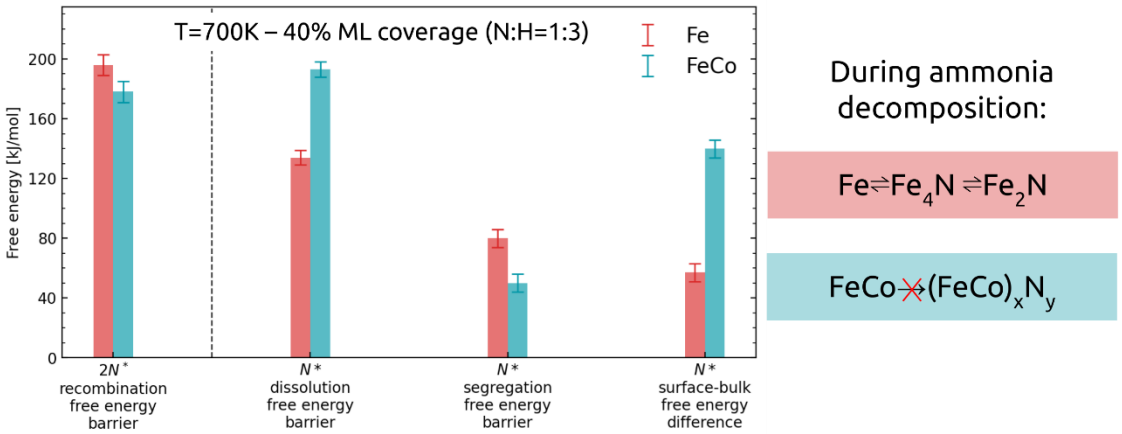


Figure 1 Free energies of the most relevant process on Fe and FeCo, obtained from MD simulations at 700K with a surface coverage of 40% (monolayer coverage, N to H ratio 1:3). On the left of the dotted line, the free energy barrier of the rate-limiting step while and on the right the free energy nitridation related process. These explain both the superior catalytic activity of FeCo with respect to Fe and its greater stability against nitridation.

References

1. I. Lucentini et al., *Ind. Eng. Chem. Res.*, **2021**, *60(51)*, 18560-18611.
2. M. S. Spencer, Nature **1986**, *323*, 685-687.
3. S. Perego, L. Bonati, S. Tripathi, M. Parrinello, *ACS Catal*. **2024**, *14(19)*, 14652-14664.
4. M. Purcel, S. Berendts, S. Perego, et al., *ACS Catal*. **2024**, *14(18)*, 13947-13957
5. S. Chen, J. Jelic, et al., Nat. Commun. **2024**, *15*, 871.
6. L. Bonati, D. Polino, et al., PNAS, **2023**, *120(50)*, e2313023120.
7. S. Tripathi, L. Bonati, S. Perego, M. Parrinello, ACS Catal. **2024**, *14(7)*, 4944-4950.

Acknowledgements

We acknowledge support from the Data Science and Computation Facility and its Support Team at Fondazione Istituto Italiano di Tecnologia, the CINECA award under the ISCRA initiative (IscraB28_AmmoFeCo) and the Max Planck Computing and Data Facility; and the Federal Ministry of Education and Research, Germany (Bundesministerium für Bildung und Forschung, BMBF, Hydrogen flagship project: TransHyDE Forschungsverbund AmmoRef, FKZ 03HY203A) for funding.

Bio Oil Steam Reforming over Mesoporous Hexagonal and Noncapsular Ni Nanoparticle Catalyst Prepared Using Post Loading and Co-Assembly Strategy

Silmina[1], Naoko Suyama, Kenji Kamiya and Eika W. Qian[*]
[1]Tokyo University of Agriculture and Technology, Graduate School of Bio-Applications and Systems Engineering, Nakacho, 2-24-16, Koganei, Tokyo 184-8588, Japan
** e-mail corresponding: whqian@cc.tuat.ac.jp*

Significance and Relevance

A series of Nickel (Ni) nanoparticle catalysts encapsulated on Al_2O_3/SBA-15 and Al_2O_3/CNFs were prepared using a post loading strategy and co-assembly strategy, respectively. The novel approach addressed the potential Ni sintering issue during bio-oil steam reforming activity. Also, the CeO_2 was introduced to prevent coke formation. Both of post loading and co-assembly strategy could reached H_2 yield up to 75%. Further, the addition of CeO_2 improved H_2 yield up to 85%. Confirming that the mesoporous hexagonal and noncapsular catalyst design types could reach high H_2 and stability.

Preferred and 2nd choice for the topic: H_2 storage and transportation, green H_2 production, hydrogen vectors (1st), Fundamental advances in understanding catalysis (2nd)
Preferred presentation: (~~Oral only~~ / Oral preferred or Short Oral / ~~Poster~~)

Introduction and Motivations

Steam reforming of bio-oil is possible to produce H_2 in large quantity, which has drawn wide attention in green energy. Acetic acid is frequently utilized as a model compound in steam reforming of bio-oil due to non-flammable, easy to store and much safe hydrogen carrier. Steam reforming of acetic acid has been extensively studied using a nickel (Ni) nonnoble-based catalyst with high activity due to its lower cost and higher availability compared to another noble-based catalyst. However, metal sintering and carbon deposition (coke) formation during the steam reforming reaction triggered catalytic deactivation in Ni-based catalysts. Based on previous studies, Ni nanoparticle catalyst needs support to stabilize Ni and enhance the catalytic activity. For instance, Ni catalyst prepared with Al_2O_3, most frequently used support, could reach high H_2 but still struggle with the catalyst deactivation.[1]

Recently, several prepared catalyst have been utilized to prevent coke formation and agglomeration of Ni, including combining Ni/Al_2O_3 into SBA-15, as a silica support due to its mesopores properties.[2,3] Further, the introduction of ceria (CeO_2), a promoter, could also help inhibit coke formation due to its rich oxygen storage capacity.[1] In fact, the strategy to prepare catalyst is crucial to obtain the final catalyst design with high diffusion through higher pore distribution inside catalyst, such as post loading strategy and co assembly strategy, these can be used due to precisely controlled Ni nanoparticle size, convenient, simple, and high stability,[2] which still lack applied in steam reforming of acetic acid. Besides, cellulose nanofibers (CNFs), a recent advances material in functional template, are a sustainable resource for templating, can be easily remove through thermal treatment, display high specific surface area, and easy in modification.[4] Combining Ni nanoparticle with CNFs as template, and after that coating it with Al_2O_3 could prevent Ni sintering, improve diffusion, and enhance activity.

Hence, in this research, Ni nanoparticle encapsulated on Al_2O_3/SBA-15 was prepared through a post loading strategy. As comparison with difference catalyst design, Ni nanoparticle coated on Al_2O_3/CNFs was prepared through co-assembly strategy. To more comprehensive study, the difference in molecular Ni precursor use, Ni(acac)$_2$ as organic and Ni(NO$_3$)$_2$ as inorganic was studied as well, including the introduction of CeO_2. The characterization and mechanism of the prepared catalysts are also investigated.

Materials and Methods

Ni#Al_2O_3/SBA-15 catalyst was prepared using the post-loading strategy. Firstly, mesoporous silica (SBA-15) support was pre-synthesized using the triblock copolymer synthesis. Then, the prepared Ni nanoparticle, CeO_2, and Al_2O_3 were loaded into the prepared SBA-15. On the other hand,

Ni@Al_2O_3/CNFs catalyst was prepared using the co-assembly strategy. At the same time, CNFs was prepared using TEMPO oxidation method to reach high carboxylate content. Followed by the loading of Ni nanoparticle, and Al_2O_3 into the CNFs. Both of prepared catalyst types were calcined at 600 °C for 6 h and molder (290-425 m) at 40 MPa.

Catalytic activity test was conducted through the prepared catalyst loaded into a fixed-bed flow reactor. Firstly, the catalyst underwent pre-treatment, including a 3 h H_2 reduction at 600°C followed by a 2 h steam treatment for passivation. Subsequently, steam reforming of acetic acid was performed. The reaction pressure was 0.1 MPa, and the reaction temperature was 650°C. The gas (GC-TCD) and liquid (GC-FID) products were analyzed.

Results and Discussion

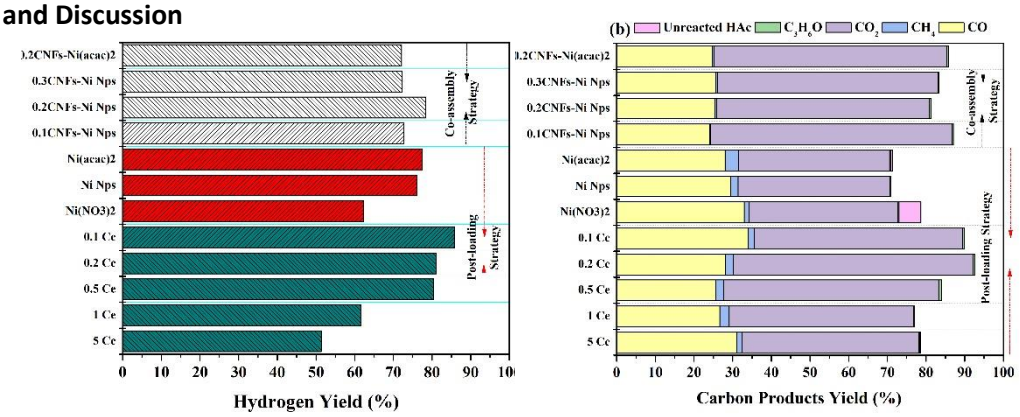


Figure 1 Steam reforming of acetic acid over prepared catalyst. (a) H_2 yield and (b) carbon product yield. Reaction condition 650 °C, S/C= 3.17, and WHSV= 21 h^{-1}

Fig. 1 reveals H_2 and carbon-based product yield of acetic acid steam reforming using post-loading strategy and co-assembly strategy, respectively. Both of prepared catalyst obtained H_2 yield up to 75%, in term of specific condition (Fig. 1a). To interpret differently of each strategy, firstly- mesoporous hexagonal catalyst design obtained by post loading strategy showed that molecular $Ni(acac)_2$ precursor received the better activity test than $Ni(NO_3)_2$ due to a higher number of active Ni nanoparticle sites (proven in H_2-TPR analysis). Further, Ni nanoparticle catalyst (Independently prepared using $Ni(acac)_2$ precursor) shown the more stability in activity test than the molecular $Ni(acac)_2$ (Fig. 1b). The addition of CeO_2 revealed that the catalyst with 0.1 wt.% of CeO_2 exhibited superior performance of H_2 yield and carbon-based product compared to higher loadings (up to 1 -5 wt.%) (Fig 1ab), confirming that at the optimum loading of CeO_2 could improve the water gas shift reaction in steam reforming. Next, through co-assembly strategy, noncapsular catalyst design, H_2 yield was achieved optimum with 0.2 g CNFs loading compared to other loadings (0.1 and 0.3 g). The addition of hard template, CNFs, impacted the activity test due to the obtained balance of surface area, pore volume and pore diameter (proven by BET analysis). Hence, directly speaking, the steam reforming of acetic acid using Ni nanoparticle encapsulated on CeO_2/Al_2O_3/SBA-15 and Al_2O_3/CNFs prepared catalyst was successfully conducted using a fixed bed flow reactor.

References

1. Pu, J. et al. *International Journal of Hydrogen Energy*, **2018**, 43, 3142-3153.
2. Zhang, W. et.al. *Advanced Materials Interfaces*, **2020**, 9(3), 2101528.
3. Shen, M. et al. *53rd Petroleum-Petrochemical Symposium of JPI. Osaka Conv. of JPI*, **2023**.
4. Park, J., et.al. *Rsc Advances*, **2024**, 14(45), 32852-32862

Acknowledgements

……

Decomposition of N_2O on Redox Tuned Cobalt Spinel Catalysts – Molecular Orbital Resolution of Reaction Mechanism

Leszek NOWAKOWSKI, Camillo HUDY, Filip ZASADA, Zbigniew SOJKA*

Faculty of Chemistry Jagiellonian University, ul. Gronostajowa 2, 30-387 Krakow, Poland

** e-mail corresponding sojka@chemia.uj.edu.pl*

Significance and Relevance

The key factors governing the redox activity of the cobalt spinel catalyst in N_2O decomposition were established. The crucial role of interactions between the virtual LUMO of N_2O and the SOMO of O_2^- with cobalt 3d orbitals, and the Fermi level position were found to play a crucial role in shuttling the electrons between the reactants and the cobalt active sites was shown for the first time. The proposed original conceptual molecular framework allows for a concise interpretation of the multifaceted redox features of the N_2O decomposition on p-type semiconductor catalysts.

Introduction and Motivations

Nitrous oxide belongs to the most important greenhouse gases, and the main sources of its anthropogenic emissions include nitric acid industry, transport, and agriculture. Despite the stoichiometric simplicity of the N_2O decomposition over oxide catalysts, the mechanism of this reaction can often exhibit a complex nature. In the present study, we address these points for catalytic N_2O decomposition, choosing well-defined cobalt spinel of the nanocubic shape and its Li and K-doped derivatives as dedicated model catalytic systems. The aim is to evaluate the redox behavior of cobalt spinel catalysts, and reveal the effects resulting from bulk and surface doping of Co_3O_4 with lithium and potassium, introduced alone or jointly. The resulting controlled electronic structure perturbations of the cobalt spinel matrix allow for straightforward clarification of the observed changes in the catalytic activity in terms of the interfacial orbital interactions, the Fermi level, and surface electrostatics variation, playing the key function.

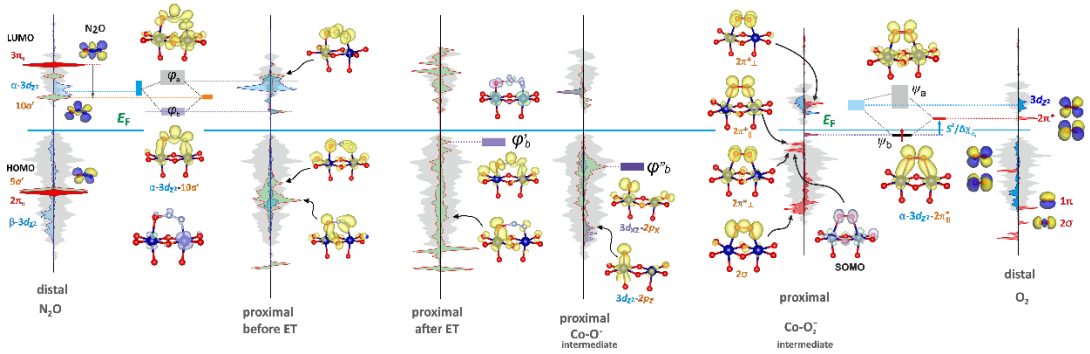
Materials and Methods

Two series of singly and doubly (Li and K) doped Co_3O_4 catalysts of a well-cut nanocube shape were synthesized. For the catalyst obtained by one-pot hydrothermal synthesis (h-$Li_xCo_{3-x}O_4$ series), lithiation of the Co_3O_4 leads to the formation of $\{Li'_{8a}, Co^{\cdot}_{16d}\}$ defects, decreasing steadily the work function and the catalytic activity. In contrast, for the catalysts prepared by post-synthesis impregnation (i-$Li_xCo_3O_4$), the formation of $\{Li'_{8a}, Co'_{16d}, Co^{\cdot\cdot}_{16c}\}$ defects leads to a volcano-type dependence of the catalytic activity, paralleled by the work function changes. Post-synthesis surface doping of the bare and lithiated spinel catalyst with potassium was achieved by dry impregnation with aqueous solution of KNO_3 (singly, i-K_y/Co_3O_4, and doubly doped i-$K_y/Li_xCo_3O_4$ series). All catalysts were thoroughly characterized by XAFS, XRD, XRF, XPS, RS, SEM, S/TEM/EDX, and Kelvin Probe techniques (work function measurements). Catalytic activity and the N_2O turnover frequencies were determined using TPSR and steady-state isothermal catalytic tests. Molecular orbital interpretation of the results was based on DFT modeling including Projected Crystal Orbital Hamilton Population (pCOHP) analysis of the catalyst|reactants electronic structure.

Results and Discussion

In the case of the i-$Li_xCo_3O_4$ series, a non-monotonous dependence of the N_2O conversion on the Li content was found. All the catalysts were more active than the parent Co_3O_4 and the h-$Li_xCo_{3-x}O_4$ catalysts, which were noticeably less sensitive to the doping level. For the h-$Li_xCo_{3-x}O_4$ catalysts, the

ΔE_a values increase steadily with the Li doping level. Yet, in the case of the i-$Li_xCo_3O_4$ series the activation energy passes through a well-pronounced minimum, revealing a dramatically opposite catalytic behavior in response to the spinel redox tuning, which is governed by the route the lithium dopant was introduced and its concentration as well. Furthermore, the activation energies exhibit a striking sensitivity to the N_2O pressure, which for the most active i-$Li_xCo_3O_4$ is almost doubled upon passing from $pN_2O \rightarrow 0$ hPa (ΔE_a = 0.66 eV) to 50 hPa (E_a =1.16). This behavior was associated with the buildup of negatively charged oxygen intermediates, since the resultant surface electrostatic field strongly influences the dynamics of the redox processes. The associated variation of the TOF values is directly correlated with the work function of the catalysts. For h-$Li_xCo_{3-x}O_4$ catalysts formation of the {Li'_{8a}, $Co^{\bullet}_{16d}$} defects decreases the work function due to the E_F energy lowering (TOF decreases), while for the i-$Li_xCo_3O_4$ catalyst, the formation of {Li'_{8a}, Co'_{16d}, $Co^{\cdot\cdot}_{16c}$} defects leads to an increase in the E_F level and the resultant lowering of the work function (TOF increases). The performance of the doubly promoted i-$K_y/Li_xCo_3O_4$ catalysts significantly outperforms those of the singly doped i-$Li_xCo_3O_4$, and i-K_y/Co_3O_4 counterparts, revealing a clear synergy of the lithium and potassium doping when both are introduced by the impregnation. The experimental results obtained, complemented by the DFT calculations, allowed us to construct a conceptual molecular orbital model of the redox interactions between the spinel catalysts and the N_2O and O_2 reactant molecules. In the proposed treatment, the conceivable redox steps of nitrous oxide decomposition, $2N_2O+2e \rightarrow [2O^-_{(ads)} \rightarrow O_2^{2-}{}_{(ads)} -e \rightarrow O_2^-{}_{(ads)}] -e \rightarrow O_{2(g)} + N_{2(g)}$, are restricted to the two key molecular events of an initial dissociative reduction of N_2O (entrance into the catalytic cycle through an interfacial electron transfer, and a terminal evolution of O_2 (exit from the catalytic cycle upon back electron transfer). Redox interactions governing the catalyst activity depend critically on the surface DOS structure and the manifold of the FMO energy levels of the reactants and intermediates involved. The corresponding lineup of the (100) surface DOS features and the $3dz^2$ orbital of Cobalt in particular with the frontier orbitals of the N_2O and O_2 reactant, and molecular orbital evolution during the principal reaction steps are shown in Figure below.



The established molecular orbital pattern, and the position of the Fermi level (E_F- blue line) control the trade-off between the interfacial electron transfer that triggers N_2O dissociation into the prime Co-$O^-_{(ads)}$ intermediates and $N_{2(g)}$, and the back electron transfer that drives the subsequent oxidative evolution of the secondary Co–O_2^- intermediates into final $O_{2(g)}$. The crucial role of overlap between the virtual LUMO 10a' and $3dz^2$ orbitals in attaining the transference of electrons between the N_2O reactant (acceptor center) and the octahedral cobalt active sites (donor center) and the pivotal function of the E_F position in the N_2O decomposition process was conceptually ascertained thereby.

The constructed molecular framework allows for a concise account of the multifaceted redox features of the N_2O decomposition on cobalt spinel catalysts. It extends the classic picture of catalysis on semiconductors, pioneered by Wolkenstein and Hauffe, primarily by including a key hybridization of the molecular orbitals of the reacting species with the catalysts DOS features (3d), surface electrostatics (buildup of O^- /O_2^- intermediates), and reorganization energy of the reactants. The proposed model of redox behavior of singly and doubly doped cobalt spinel can be applied to any type of oxide catalysts, often used in fundamental studies and practical deN_2O applications, for straightforward molecular orbital rationalization of the structure-redox reactivity relationships.

Monitoring the active site of CeO_2 supported Pd by H_2-D_2 exchange and EXAFS

Felix Ott[1], Chalachew Mebrahtu[1,2], Regina Palkovits[*1,2]
[1]*Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany*
[2]*Institute for Sustainable Hydrogen Economy, Forschungszentrum Jülich GmbH, Jülich, Germany*
* palkovits@itmc.rwth-aachen.de, r.palkovits@fz-juelich.de

Significance and Relevance

In this work we present an investigation of the structure-activity relationship of CeO_2 supported Pd-containing catalysts using H_2-D_2 exchange in combination with EXAFS and the main goal is to monitor the presence of either single atoms or nanoparticles of Pd. The approach was first reported by our group and is further refined, applied for metal oxide-supported catalysts, which previously were difficult to investigate for the presence of single atoms.

Preferred and 2nd choice for the topic: *1st Fundamental advances in understanding catalysis*
2nd Automotive and stationary emission control
Preferred presentation: oral preferred or short oral

Introduction and Motivations

Single atom catalysis represents a promising approach in optimizing noble metal usage, while also offering different performances in terms of activity and/or selectivity compared to bulk or nanoparticles. However, information and knowledge about the structure of alleged single atom catalysts are lacking and difficult to obtain. This is due to the often low amounts of noble metal used, the need for costly analytical methods, such as XAS, and operating these analytical methods at the detection limit. As a result, new approaches are required, which simplify and adapt the process of investigating the structure-activity relationship of single atom catalysts. The main approach is based on the H_2-D_2 exchange in combination with XAS based on the study by *Vennewald et al.*, which reported the inactivity of Pd-single atoms (Pd-SA) compared to Pd-nanoparticles on graphitic carbon nitrides in the H_2-D_2 exchange up to 200°C.[1]

Materials and Methods

In this work, we investigate Pd/CeO_2 and Pd-Cu/CeO_2 using H_2-D_2 exchange in combination with XAS to collect information about the structure and performance of these materials. Moreover, NO reduction with hydrogen was performed to evaluate potential application in hydrogenation reactions.

Results and Discussion

The main methodologies employed consist of the H_2-D_2 exchange and synchrotron based XAS experiments at the Diamond Light source. In the first step, all materials were tested in the H_2-D_2 exchange up to 200°C with either non-reductive or reductive pretreatment conditions. Based on these experiments certain points of interest were determined and chosen for synchrotron experiments, which revealed the structure and changes of the materials. Exemplary of the obtained results for Pd/CeO_2 are shown in Figure 1. During a non-reductive pretreatment, the material does not show activity in the H_2-D_2-exchange starting at 50°C and following a reductive pretreatment, the material catalysed HD formation starting at 50°C (Fig. 1 left). As reported in the literature, this hints towards the lack of Pd-NP (NP: Nanoparticles) for the untreated samples and the formation of Pd-NP during pretreatment or reaction. Fig. 1 right depicts the EXAFS results for Pd/CeO_2, which shows the bond interaction of Pd with its neighbouring atoms. The lack of Pd-Pd bonds in combination with the presence of Pd-O and Pd-Ce bonds is a clear indicator for the presence of Pd-SA in CeO_2 in pristine samples and in line with the H_2-D_2 results.[2-4] Following the pretreatment, Pd-Pd bonds emerge, which further confirm the theories based on the H_2-D_2 results. Interestingly in the case of Pd-Cu/CeO_2, Pd also is present as Pd-SA on CeO_2 with no interaction with Cu in pristine conditions and also starts to develop Pd-NP following a treatment. Yet, for this material, an influence of the Pd-Cu bond starts to

emerge following the reductive pretreatment, which might explain differences in the H_2-D_2 results (see Fig 1. Left).

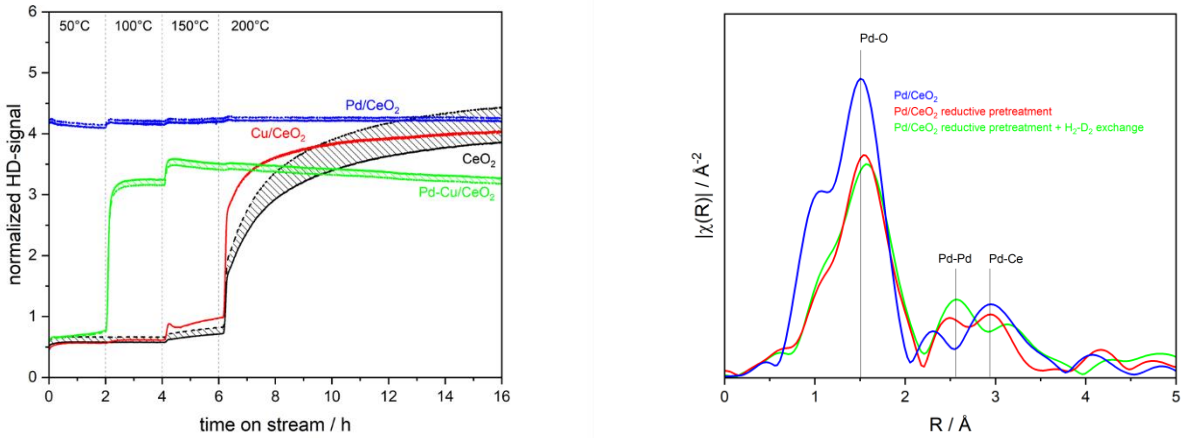


Figure 1. Normalized-HD signals of Pd-Cu/CeO_2, Pd/CeO_2, Cu/CeO_2 and CeO_2 in the H_2-D_2 exchange after a reductive pretreatment (left). And normalized magnitudes of the k-weighted Fourier transform (FT) of the extended X-ray absorption fine structure spectra in radial distance (not phase corrected) for Pd/CeO_2 (right). Normalization and correction of the HD signals are based on either H_2- (full lines) or D_2- (dashed lines) base-conversion rates. Reaction conditions: 2% D_2, 2% H_2, 96% Ar, GHSV = 20000 – 55000 h^{-1}; Pretreatment non-reductive condition: 100% Ar, 50 °C, 2 h; Pretreatment reductive condition: 2% H_2, 98% Ar, 550 °C, 2 h.

Additional experiments were conducted for Pd/CeO_2 in the NO reduction using H_2, which further highlights the importance of understanding the active species for given reactions, as the material containing Pd-NP shows higher activity and N_2 selectivity overall and at lower temperatures.
In conclusion, it can be said that the H_2-D_2 exchange proves to be a simple, yet highly sensitive method for obtaining hints about the Pd active species formed during different treatment conditions. Although, H_2-D_2 does not stand alone as a verification method for the formation of single atom or nanoparticle but supports more complex methods and limits the experimental effort required.

References

1. M. Vennewald, N. M. Sackers, A. Iemhoff, I. Kappel, C. Weidenthaler, A. Meise, M. Heggen, R. E. Dunin-Borkowski, L. Keenan, R. Palkovits, Journal of Catalysis **2023**, *421*, 134.
2. T. Fujikawa, K. Tsuji, H. Mizuguchi, H. Godo, K. Idei, K. Usui, Catalysis Letters, **1999**, *63*, 27.
3. X. Wang, J. Chen, J. Zeng, Q. Wang, Z. Li, R. Qin, C. Wu, Z. Xie, L. Zheng, Nanoscale **2017**, *9*, 6643.
4. F. Xing, J. Jeon, T. Toyao, K.-I. Shimizu, S. Furukawa, Chemical science **2019**, *10*, 8292.
5. Felix Ott, Chalachew Mebrahtu, Julia Nikodemus, Gunjana Yadav, Luke Keenan, Abhishek Khetan, Regina Palkovits, **2024** manuscript in preparation

Acknowledgements

This project was funded by the Cluster of Excellence Fuel Science Center (EXC 2186, ID: 390919832) by the Excellence Initiative by the German federal and state governments to promote science and research at German universities. We would like to thank Diamond Light source for synchrotron measurements.

Deconvolving the Standard-SCR Redox Mechanism on Copper-Zeolites for Catalyst Insight and Development

Andrea *GJETJA*[1], Nicola USBERTI[1], Nicole Daniela NASELLO[1], Umberto IACOBONE[1], Isabella NOVA[1], Enrico TRONCONI[*,1], Roberta VILLAMAINA[2], Maria Pia RUGGERI[2], Djamela BOUNECHADA[2], Andrew P. E. YORK[2], Jillian COLLIER[2]

[1]*Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, Via La Masa, 34, 20156 Milan, Italy*

[2]*Johnson Matthey Technology Centre, Blounts Court Road, Sonning Common, Reading RG4 9NH, UK*

*enrico.tronconi@polimi.it

Significance and Relevance

We investigates NH_3-SCR over Cu-CHA zeolite catalysts, the state-of-the-art technology for NO_x abatement in Diesel vehicles. By independently studying the two redox half-cycles of Standard-SCR using transient kinetic analysis, we assess the role of copper redox state (Cu^{II}/Cu^{I}) and clarify so far controversial effects of water feed content, hydrothermal aging, and catalyst formulation on the Standard-SCR activity, enabling improved predictions of the steady-state NO_x conversion. These findings help to optimize the SCR catalysts, contributing to enhanced DeNOx performance of emissions control technologies for cleaner Diesel vehicles.

Preferred and 2nd choice for the topic: Fundamental advances in understanding catalysis (or Automotive and stationary emission control)
Preferred presentation: *Oral only*

Introduction and Motivations

Ammonia-Selective Catalytic Reduction (NH_3-SCR) is the state-of-the-art aftertreatment technology for Diesel-fuelled vehicles complying with Euro 6/7 standards. These systems nowadays implement copper-exchanged zeolite catalysts, which exhibit high DeNOx activity in a wide temperature range, high selectivity to N_2 and good hydrothermal stability. The Standard-SCR ($4\ \ +4\ \ _3+\ \ _2\rightarrow 4\ \ _2+6\ \ _2$) reaction mechanism, however, is still debated and not fully understood, even though a general consensus on a Cu redox mechanism has been reached. To convert NO to N_2, copper is reduced from Cu^{II} to Cu^{I} in the Reduction Half-Cycle (RHC)[1]. Then, to restore the activity of the catalyst, the Cu^{I} sites are oxidized back to Cu^{II} by oxygen only in the Oxidation Half-Cycle (OHC)[2].

The transient response approach proposed by our group enables to study independently the kinetics of the two half-cycles, which are then combined to predict the Standard-SCR steady-state performances[3]. Herein we show that by separately assessing the impact of operating conditions and catalyst parameters, such as H_2O presence, catalyst hydrothermal aging, zeolite SAR and Cu loading, on the rates of the two half-cycles, we can clarify so far confusing and controversial effects on the overall Standard-SCR activity at steady state.

Materials and Methods

We have tested Cu-Chabazite (Cu-CHA) catalysts characterized by different exchanged-copper contents (between 0.8 and 2.3 wt%), silica-to-alumina ratios (SAR, between 10 and 25), and Hydrothermal Aging extents (HTA, conditioned or aged). In addition, different reaction conditions have been explored: H_2O presence (0-2 v%), NO feed concentration (300-500 ppm), O_2 concentration (1-8 v%) and temperature (135-500 °C). The reference catalyst was Cu = 1.8 wt% and SAR = 25 (called 1.8Cu-CHA25).

Transient kinetic tests have been run to study independently the RHC (feeding equimolar concentrations of NO and NH_3), the OHC (by oxidizing the sample with O_2 across different time intervals), and the Standard-SCR reaction ($NO+NH_3+O_2$ feed, followed by oxygen removal to titrate the bed-average steady-state oxidized copper fraction)[3]. More experimental details are provided in [3].

A UV gas analyser and a mass spectrometer are used to monitor the temporal evolution of the gas species concentrations. These data undergo Transient Kinetic Analysis (TKA) based on a plug flow reactor model, implemented as a cascade of 20 CSTRs. This model includes the following rate equations for the RHC and OHC[3]:

$$(1) \qquad = \left(\frac{\quad}{\quad}\right)^{\ 2} \qquad (2) \qquad = \left(\frac{\quad^{2}}{\quad}\right)(1-\ \ )^{2}$$

where are the respective rate constants, are the molar fractions, $= 500$, $_2^{\ 2} = 8\ \%$, and is the fraction of oxidized copper sites.

Results and Discussion

For each catalyst sample, TKA of the transient data collected in both reduction and oxidation conditions is performed to estimate the rate constants for RHC and OHC, respectively. is estimated by fitting the NO and N_2 dynamics during the RHC transients. Instead, is obtained from the evolution in time of the oxidized copper fraction during the OHC runs. Figure 1a) and 1b) show the RHC and OHC rate constants for the 1.8Cu-CHA25 catalyst in wet and dry feed conditions (2 and 0 v% H_2O, respectively). Over this sample, H_2O has a modest inhibiting effect on RHC, but a stronger promoting effect on OHC.

Fig. 1c and 1d show that, by combining these two independently estimated rate constants, it is possible to predict with good accuracy both the NO conversion and the bed-average oxidized Cu fraction at Standard-SCR steady state in both dry and wet conditions. Furthermore, the estimated rate constants correctly predict the slightly improved NO conversion and the incremented oxidized copper fraction in wet conditions. Studying just the steady-state activity would lead instead to the erroneous conclusion that H_2O has no significant impact on Standard SCR.

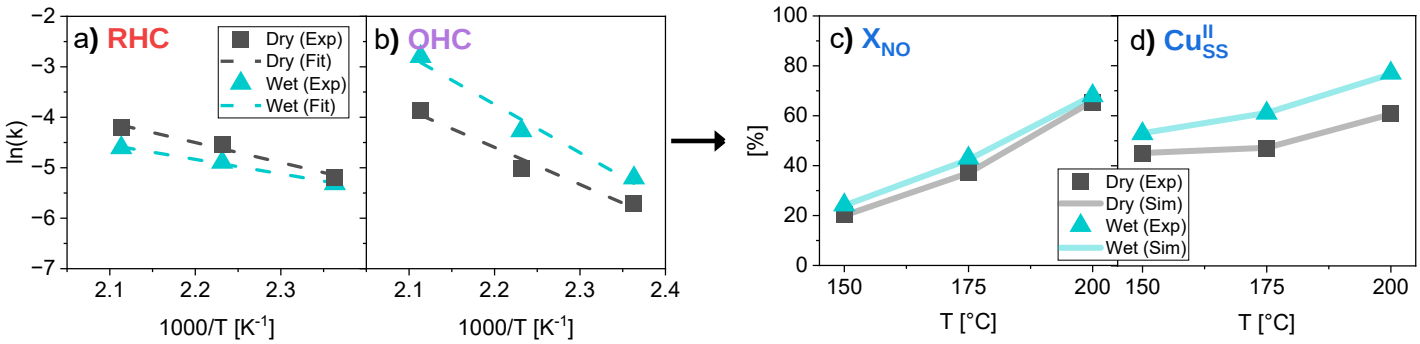


Figure 1 a) RHC rate constants, b) OHC rate constants, c) NO conversion and d) bed-average steady-state oxidized copper fraction. 2Cu-CHA25 sample. Dry and wet conditions: H_2O=0-2 v%, grey squares and blue triangles, respectively. Dotted lines for kinetic fits and transparent solid line for simulations. Feed: NO = NH_3 = 500 ppm and O_2 = 8% in He. T-range = 150-200 °C. W_{cat} = 32 mg, Q = 240 cm^3/min (STP)

A similar methodology has been applied to elucidate the effects of hydrothermal aging, zeolite SAR, and Cu loading in Cu-CHA. HTA does not affect RHC, while it inhibits the OHC, thus determining a loss in both NO conversion and Cu^{II} fraction at Standard SCR steady state. Decreasing SAR (higher aluminium content) promotes RHC but leaves OHC unchanged, thus leading to higher NO conversions but to decreased oxidized Cu fractions at steady state. On incrementing the Cu loading, a strong OHC promotion is apparent, while the effect on the RHC is more complex.

Finally, on extending the experimental and modelling analysis to temperatures above 220°C we have found that the well-known "seagull" shape of the NO light-off curves typical of Cu-CHA catalysts is associated with a drop of the OHC rates between 250 and 350 °C. On the contrary, the RHC rates increased monotonically with increasing temperature, following a regular Arrhenius trend.

In conclusion, our original methodology based on decoupling the RHC and the OHC of the Standard-SCR redox mechanism by transient methods can provide valuable phenomenological insight into the effects of reaction variables and catalyst formulation parameters. Such effects, which are clearly distinct (and often opposite) for the two half cycles of the SCR redox mechanism, would remain inaccessible if focusing only on steady-state activity data.

References

1. F. Gramigni, N. D. Nasello, N. Usberti, U. Iacobone, T. Selleri, W. Hu, S. Liu, X. Gao, I. Nova, E. Tronconi, *ACS Catalysis* **2021**, *11, 8*, 4821-4831
2. R. Daya, D. Trandal, U. Menon, D. J. Deka, W. P. Partridge, S. Joshi, *ACS Catalysis* **2022**, *12, 11*, 6418–6433.
3. N. D. Nasello, U. Iacobone, N. Usberti, A. Gjetja, I. Nova, E. Tronconi, R. Villamaina, M. P. Ruggeri, D. Bounechada, A. P. E. York, J. Collier, *ACS Catalysis* **2024**, *14, 6*, 4265-4276.

Acknowledgements

This work was financially supported by Johnson Matthey.

Powerful CO_2 methanation system by electrically heating spiral-type structured catalyst

Ryo Watanabe, Kohki Nishide, Hiroshi Akama, Choji Fukuhara*
Department of Applied Chemistry and Biochemical Engineering, Graduate School of Engineering, Shizuoka University, 3-5-1 Johoku, Chuo-ku, Hamamatsu, Shizuoka, Japan
** fukuhara.choji@shizuoka.ac.jp*

Significance and Relevance

This study demonstrates an innovative CO_2 methanation system using a spiral- type structured catalyst, which is directly heated by an electric current. The constructed methanation system indicated a powerful and stable performance even under a severe condition. Infrared imaging confirmed a desirable temperature profile with uniform distribution along with the spiral shape. Notably, the optimization of the spiral shape such as a twisting angle degree significantly affected on the methanation performance. Long-term stability tests confirmed CO_2 conversion over 50 hours at 350 °C.

Introduction and Motivations

The CO_2 methanation reaction ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$) has gained attention as a key technology for Carbon Capture and Utilization (CCU), allowing the conversion of CO_2 into valuable methane. Our research group focuses on the industrial implementation of this reaction, particularly for flue gas, which typically contains oxygen that can degrade catalysts through oxidation. However, we have discovered that oxygen can enhance CO_2 methanation.[1,2] The presence of oxygen induces an auto-methanation (AM) process, where the combustion of hydrogen and oxygen generates internal heating in the reactor, driving the methanation reaction without external heating. This internal heating increases energy efficiency. A key innovation in this research is the use of spiral catalysts, which are commonly used to improve heat transfer in catalytic systems. These catalysts facilitate the efficient delivery of thermal energy to the reaction site through the swirling flow of the gas. The metallic helical base material of the catalyst enhances heat conduction, which significantly improves reaction efficiency.

In this study, we present a new method of internal heating called 'electrical heating' (*e*-reaction), where the catalyst itself is powered by electricity and generates reaction heat by Joule heating. The schematic diagram of methanation with electrical heating (*e*-methanation) system is shown in Figure 1. Spiral-type catalysts, typically made of relatively high-resistance Ni-Cr metals, are ideal for this purpose. When an electric current is applied, the catalyst forms a heated reaction field. This method allows a uniform temperature distribution within the reactor, achieving rapid heating and improving reaction efficiency, potentially at lower power input. Thus, in this study, the reaction characteristics of the e-methanation system were investigated, as well as the effect of twisting angle of the spiral catalyst. In addition, the durability of the system was evaluated.

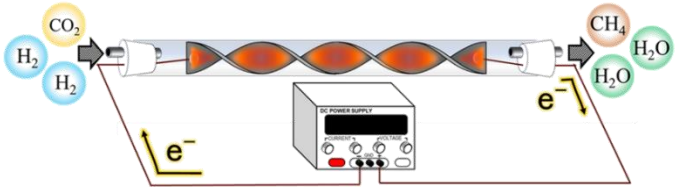


Figure 1 Schematic diagram of e-reaction system.

Materials and Methods

A wash-coat method was used to prepare the spiral-shaped catalysts. Ru/CeO_2 powder was obtained by impregnating and calcining the Ru component onto a CeO_2 substrate with a 10 wt% Ru loading. The powder catalyst was then suspended in distilled water, and a spiral substrate (11 mm wide × 180 mm long) twisted to 720° was immersed in the suspension and dried overnight. The spiral base material is a porous metal with continuous pores. This spiral base material was dipped and dried several times to obtain a spiral-shaped catalyst with a coating weight of 1.0 g·piece^{-1}.

The catalyst underwent hydrogen reduction at 200 °C for 60 min. The temperature was subsequently increased by applying 10 W of power in an N_2 atmosphere. When a constant temperature

was reached, the reaction gas was supplied. The power was gradually decreased when the reaction reached a steady state.

Results and Discussion

Figure 2 shows the CO_2 conversion and average temperature of the spiral catalyst when the power input, initially 10 W, was gradually reduced to 5 W. The average measured temperature at each position (expressed as the average temperature) is shown in the figure. At 10 W, the CO_2 conversion reached 80% with an average temperature of 297 °C. Subsequently, the power input was gradually reduced. Even at 5 W, the CO_2 conversion remained high at 75%, with an average temperature of 210 °C, approximately 90 °C lower than at 10 W.

Figure 3 shows the effect of varying the twist angle (0°–1080°) on methane conversion properties for plate and spiral catalysts. Higher twist angles led to increased CO_2 conversion, likely due to stronger swirl flow on the catalyst surface, improving methanation efficiency. Spiral heat exchangers are effective heat conductors, with their geometry promoting swirl flow, reducing boundary film resistance, and increasing the heat transfer coefficient. The induced turbulent gas flow thins the boundary layer, a major factor in increasing heat exchange efficiency. Therefore, higher twist angles increase methanation efficiency by lowering gas boundary films. The fact of no significant difference in reactivity with increasing angle is predicted to indicate that the swirling effect is sufficient at 360° of twist angle. It is expected that the effect of twist angle would be demonstrated under conditions where the effect of mass transfer is significant.

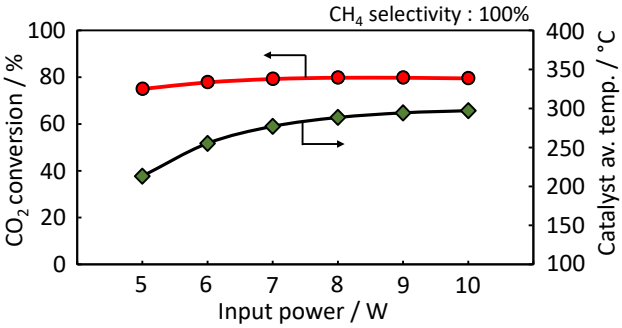


Figure 2 CO_2 conversion and average temperature of catalyst at each power input power.

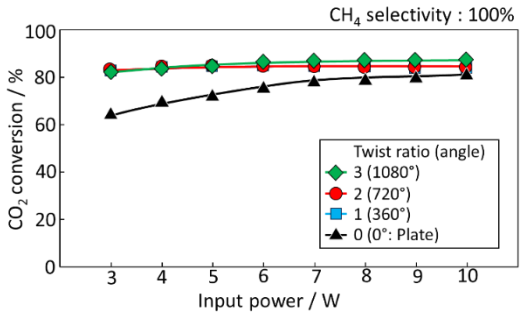


Figure 3 CO_2 conversion of spiral structured catalyst at an initial power input of 10 W.

Figure 4 shows the results of the e-methanation over an extended period, with power input fixed at 5 W and the reaction characteristics evaluated after 50 h. In the early stages of the reaction, a slight decrease in conversion was observed, but the performance remained almost constant. The average temperature of the reaction field was maintained at 350 °C. This consistent temperature, maintained by the effective current flow through the substrate and the swirling flow generated by the spiral shape of the catalyst bed, providing a sufficient downstream heating of the catalyst bed and high conversion characteristics.

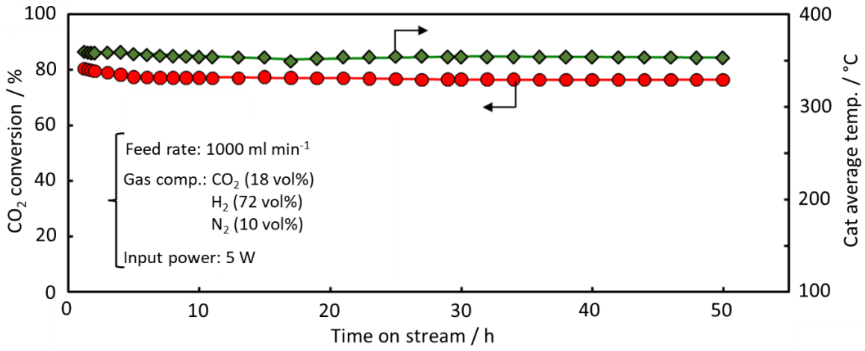


Figure 4 Durability performance for *e*-Methanation.

References

1. C. Fukuhara, S. Ratchahat, Y. Suzuki, M. Sudoh, R. Watanabe, *Chemistry Letters,* **2019**, *48(3)*, 196.
2. N. Hirata, R. Watanabe, C. Fukuhara, *Fuel,* **2020**, *282*, 118619.

Acknowledgements

This work was supported by JST-ALCA-Next Program Grant Number JPMJAN24C2, Japan.

Enhancing CO_2 Hydrogenation Efficiency through *in situ* Formation of Active Species in Carbon Nitride Modified Catalysts

Angelina BARTHELMEß,[1] Dan ZHAO,[1] Maik KAHNT,[2] Michael ZIMMERMANN,[1] Enrico TUSINI,[1] Timo VAN ROJE,[1] Cherie HSU,[1] Thomas SHEPPARD,[1] Anna ZIMINA,[1] Jan-Dierk GRUNWALDT,[1] Moritz WOLF[1*]
[1]Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen/Germany,
[2]MAX IV Laboratory, Lund/Sweden
** moritz.wolf@kit.edu*

Significance and Relevance

This research demonstrates a novel approach to enhance performance during CO_2 hydrogenation by using carbon nitride (CN) coated Al_2O_3 composites as a support material. Unlike conventional fine powdered CN, which has low surface area, the CN coating on Al_2O_3 enables tunable porosity and minimizes pressure drop in fixed-bed reactors. Co-based catalysts using CN@Al_2O_3 composites as support showed significantly increased CO_2 conversion with enhanced methane selectivity compared to the unmodified catalyst. The modification induced an activation phase with selectivity switch to CH_4 suggesting the formation of *in situ* active species.

Preferred and 2nd choice for the topic: CO2 utilization and recycling (2nd choice: Circular economy)
Preferred presentation: Oral only / Oral preferred or Short Oral

Introduction and Motivations

CO_2, the predominant greenhouse gas, requires innovative strategies to mitigate its environmental impact. Hydrogenation of CO_2 to methane and short-chain hydrocarbons offers a scalable solution compatible with existing natural gas infrastructure.[1] Earth-abundant metal catalysts (Ni, Fe, Co) on high-surface-area supports are common catalysts for this application. Herein, the support is modified by polymerized carbon nitride (CN), which has attracted considerable attention in catalysis due to its versatile photochemical properties as well as its chemical and physical characteristics, which make it an ideal photocatalyst or potential catalyst support for thermocatalysis.[2,3] CN may stabilize nanoparticles (NPs) by generating delocalized electron states that alter the electron density at the catalytically active metal centers, thereby increasing their reactivity. As an organic polymer semiconductor, CN interacts with the metal particles, causing the active phase and support to act as an integrated system rather than separate entities.[3]

Results and Discussion

This research focuses on enabling synergetic effects by using CN modified support in thermocatalytic CO_2 hydrogenation. While common fine powdered CN from melamine polymerization exhibits low surface area and minimal porosity,[3] we explore modifying Al_2O_3 with a CN coating (**Figure 1**) to create tunable porosity. These composites were created with various morphologies and structures to produce a support that can be customized in terms of its porosity. These CN@Al_2O_3 composites were investigated in terms of their structural characteristics using X-ray nano-tomographic measurements performed at NanoMAX beamline at MAX IV, Lund.[4] The aim of our project is to investigate the structural and reactive properties of CN@Al_2O_3 as a support material for the hydrogenation of CO_2 to CH_4 and short-chained hydrocarbons. Metal oxide NPs are synthesized separately[5] and immobilized on CN@Al_2O_3 composites and Al_2O_3 benchmarks.

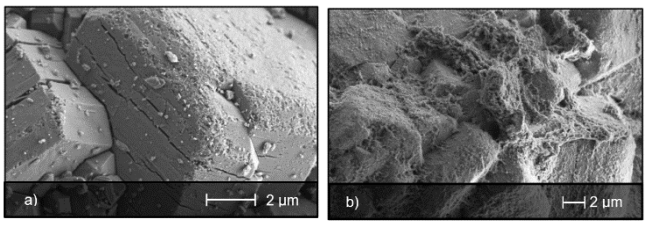


Figure 1. SEM micrographs of unmodified Al_2O_3 (a) and modified CN@Al_2O_3 support (b) with a scale of 2 µm.

Inductively coupled plasma optical emission spectroscopy (ICP-OES), N_2 physisorption, X-ray diffraction (XRD), temperature-programmed reduction (TPR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy and high-resolution solid-state ^{13}C and ^{1}H NMR spectroscopy were employed for the characterization of these materials.

After reduction of the metal oxide NPs in H_2, we obtained the M/CN@Al_2O_3 (M = Co, Fe, Ni, Cu) catalysts for comparison in CO_2 hydrogenation. For the Co/CN@Al_2O_3 catalyst, our results (**Figure 2**) reveal a significant enhancement in CO_2 conversion under moderate conditions during an activation period, which also resulted in a notable increase in methane selectivity up to 97% at 325 °C. The activation phase of modified Co catalyst was not observed for the unmodified Co/Al_2O_3 and further studied under isothermal conditions. This suggests that the CN modification facilitates the formation of *in situ* active species. *Operando* XAS measurements at the CAT-ACT beamline at ANKA at KIT[6] suggest the formation of carbide species.

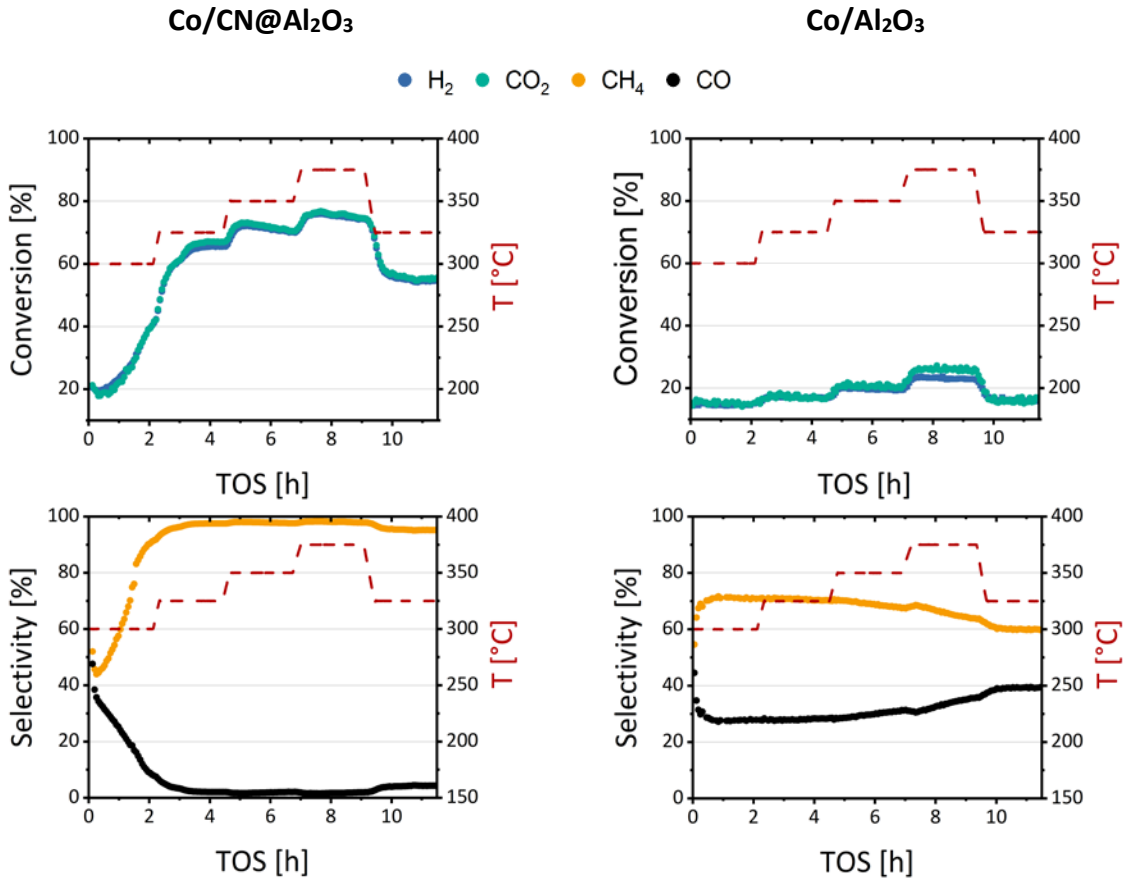


Figure 2. Conversion (top) and selectivity (bottom) in CO_2 methanation: Comparison of Co/CN@Al_2O_3 (left) and Co/Al_2O_3 (right) at 300 – 375 °C and 5 bar_g with H_2/CO_2 = 4.

References

1. K. M. K. Yu, I. Curcic, J. Gabriel, S. C. E. Tsang, *ChemSusChem* **2008**, 1, 893–899.
2. M. Antonietti, F. Goettmann, A. Thomas, *Angew. Chem. Int. Ed.* **2007**, 46, 2717–2720.
3. X.-H. Li, M. Antonietti, *Chem. Soc. Rev*. **2013**, 42, 6593–6604.
4. U. Johanson, D. Carbone, U. Vogt, *J. Synchrotron Radiat.* **2021**, 28, 1935–1947.
5. M. Wolf, N. Fischer, M. Claeys, *Mater. Chem. Phys.* **2018**, 213, 305–312.
6. A. Zimina, K. Dardenne, J.-D. Grunwaldt, Rev. Sci. Instrum. **2017**, 88, 113113.

Nickel acetylacetonate grafted on CaO-modified hydroxyapatite catalysts for enhanced performance in decarbonization processes : Effect of Ni loading

Nassima Berroug*, Miguel A. Gutiérrez-Ortiz, Juan R. González-Velasco, Zouhair Boukha
Chemical Technologies for Environmental Sustainability Group, Department of Chemical Engineering, Faculty of Science and Technology, University of the Basque Country UPV/EHU, P.O. Box 644, E-48080, Bilbao, Spain
**e-mail: nassima.berroug@ehu.eus*

Significance and Relevance

The investigated Ni-Ca-HAP grafted catalysts demonstrate a promising performance in the CO_2 methanation reaction, shedding light on their suitability and competitiveness when compared with reference materials. According to the catalytic activity results, the tested samples achieve their maximum conversion, corresponding to the thermodynamic equilibrium (TE), at relatively low temperatures ($T_{max} \leq 425$ °C).

***Preferred presentation*: (Oral only)**

Introduction and Motivations

The use of green hydrogen (GH2) as a fuel is expected to lead the energy transition, proposed as a promising alternative to traditional energy raw materials[1,2]. However, numerous issues seem to delay the application of GH2 as an energy vector at a large-scale. According to previous reports, components of available natural gas (NG) transmission and distribution networks are incompatible for GH2. Such drawbacks warrant the development of alternative solutions by using NG storage and transport facilities. In this sense, the re-utilization of CO_2, through its catalytic reaction with hydrogen for synthetic NG production, appears to be an attractive strategy.

The efficient catalysts for the CO_2 methanation reaction should be able to reach CO_2 conversions corresponding to TE at low temperatures (< 500 °C) and exhibit a high selectivity towards CH_4 formation[1,2]. In this sense, Ni-based catalysts have been widely investigated due to their high activity and low-cost. There are, however, a number of drawbacks, which appear to restrict their effective application. For instance, previous studies reported that they might suffer from a rapid deactivation due to a loss in either the number of Ni active sites or the basic sites. Therefore, many studies dealing with the design of novel formulations to provide a suitable interaction metal-support and/or to promote the surface basicity are presently available. For instance, the effect of the addition of some metal oxides (CaO, La_2O_3, CeO_2 and MgO) used as chemical promoters on the activity and stability of the catalysts has been extensively investigated. In addition to their role in providing surface basic properties, they also improve the reducibility, the dispersion of Ni NPs and, thus, their resistance against deactivation.

In this work, a series of nickel acetylacetonate $Ni(acac)_2$ grafted on CaO-modified hydroxyapatite samples are synthesized, characterized and assayed in the CO_2 methanation reaction.

Materials and Methods

The Ca-doped HAP sample presenting 2 wt.% Ca was prepared by impregnation, using a $Ca(NO_3)_2 \cdot 4 H_2O$ salt solution. The resulting sample was dried at 120 °C, for 12 h and, then, calcined at 500 °C (5 °C min^{-1}) for 4 h. The Ni-Ca-x catalysts were synthesized by grafting method. First, $Ni(acac)_2$ complex was dissolved in toluene at 60 °C. Thereafter, the solution temperature was adjusted to 30 °C and then 3 g of Ca-modified HAP support was added. The suspension was kept in isothermal conditions, under vigorous stirring, for 3 h. The grafted sample was then (i) filtered, (ii) washed with pure toluene, (iii) dried at 80 °C for 12 h and (iv) finally calcined in air for 4 h at 500 ºC (5 °C min^{-1}). The nature of the Ni-support interactions have been investigated by using several characterization techniques, including XRF, DRS, TGA, FRX, FTIR, BET, XRD, CO_2-TPD, H_2-TPR and TEM. The experiments corresponding to the CO_2 methanation reaction were performed in a tubular flow reactor (ID = 9 mm) working at atmospheric pressure. The pre-treatment of the catalysts (500 mg, 160-250 µm) consisted of their reduction at 500 °C under a 20% H_2/N_2 for 1 h and cooling to 200 °C in a flow of N_2. The reaction mixture

was composed of 16% CO_2, 64% H_2 and 20% N_2, with a total flow of 250 $cm^3\ min^{-1}$, which corresponds to a WHSV of 30,000 $cm^3\ g^{-1}\ h^{-1}$. The reaction temperature was sequentially increased, with intervals of 25 °C, from 200 to 500 °C. The analysis system consisted of a gas chromatograph (Agilent 490 Micro GC) equipped with a TCD detector.

Results and Discussion

Table 1 summarizes the chemical, textural and catalytic properties of the grafted catalysts. The efficacy of the grafting process seems to depends on the initial concentration of $Ni(acac)_2$. The progressive addition of Ni did not affect significantly the textural properties of the HAP support.

Table 1. Chemical analysis and textural properties of the grafted Ni-Ca-X samples

Muestra	FRX			BET			Activity
	Nominal wt.% Ni	Actual wt.% Ni	Grafting Yield, %	S_{BET}, $m^2\ g^{-1}$	V_p, $cm^3\ g^{-1}$	dp, nm	T_{50}, °C
HAP	-	-	-	51	0.39	27.7	-
Ni-Ca-0.26	1.9	0.59	30.3	49	0.26	19.7	322
Ni-Ca-0.39	2.9	1.03	36.0	49	0.29	21.7	310
Ni-Ca-0.52	3.8	2.04	54.1	50	0.29	21.6	287
Ni-Ca-0.65	4.7	2.50	53.7	50	0.30	21.0	284
Ni-Ca-0.78	5.5	3.59	64.9	48	0.29	20.0	286

Fig. 1 shows the light-off curves for all activated Ni-Ca-X samples in the CO_2 methanation reaction. The catalysts were previously activated in a 20% H_2/N_2 flow, at 500 °C for 1 h. The activity of Ni-Ca-0.26 sample starts at 225 ° C and increases with the reaction temperature to reach 50% conversion at 325 °C and values close to those of TE at 400 °C. The progressive addition of Ni improves the overall activity, since it systematically decreases the value of T50 (Table 1). Thus, based on the T50 values, the activity follows this general trend: Ni-Ca-0.78 > Ni-Ca-0.65 > Ni-Ca-0.52 > Ni-Ca-0.39 > Ni-Ca-0.26. In parallel, the selectivity of all catalysts approaches 100% in the range of 325-425°C (Fig. 1b). It should be highlighted that the performance of the Ni-Ca-X grafted catalysts clearly outperforms those given over impregnated Ni catalysts used as reference (not shown). This result was associated with the occurrence of suitable properties on the samples prepared by grafting method.

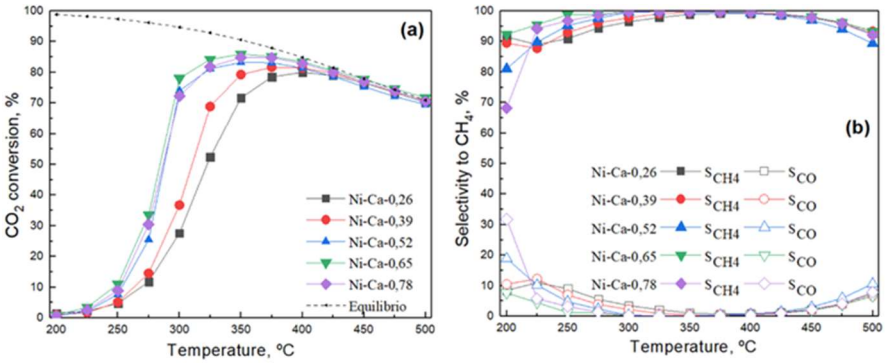


Figure 1. CO_2 conversion and selectivity to CH_4 for Ni-Ca-X grafted catalysts

References

1. Z. Boukha, A. Bermejo-López, U. De-La-Torre, J. R. González-Velasco, Appl. Catal. B-Environ. 338 (**2023**) 122989.
2. Z. Boukha, A. Bermejo-López, B. Pereda-Ayo, J. A. González-Marcos, J. R. González-Velasco, Appl. Catal. B-Environ. 314 (**2022**) 121500.

Acknowledgements

The authors are indebted to Science and Innovation Ministry (PID2019-105960RB-C21), the Basque Government (IT1509-2022) and I+D+i project CNS2022-135152 funded by MCIN/AEI/10.13039/501100011033/ and the European Union NextGenerationEU/PRTR for the financial support.

Effect of the pre-activation conditions on the nature of the active sites generated during CO_2 hydrogenation to MeOH over Cu-based catalysts

Catia CANNILLA*[1], Mariarita SANTORO[1], Serena TODARO[1], Hanna Solt[2], Ferenc Lonyi[2], Francesco ARENA[1], Giuseppe BONURA[1]

[1]*Institute of Advanced Technology for Energy CNR-ITAE, S. Lucia sopra Contesse, 5, 98126 Messina, Italy.*

[2]*Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Magyar tudósok körútja 2, H-1117, Budapest, Hungary.*

** e-mail corresponding: catia.cannilla@cnr.it*

Significance and Relevance

Considering the technologic, economic and environmental advantages, MeOH synthesis through CO_2 hydrogenation represents a promising approach to recycle CO_2 closing the carbon loop and offering an efficient route to store H_2 in an easily transportable liquid organic carrier. To achieve a comprehensive understanding of $CuZnOZrO_2$ catalysts, an integrated approach based on main morphological and structural diagnostic techniques was assessed. This provided complementary insights into their specific features enabling the correlation between catalytic performance and structural properties. Then, *in operando* DRIFT spectroscopy resulted a powerful tool for uncovering the catalytic pathways involved in MeOH synthesis, allowing the optimization of catalyst design and operative strategy.

CO_2 utilization and recycling; Fundamental advances in understanding catalysis

Oral preferred or Short Oral

Introduction and Motivations

In the frame of Carbon Capture and Utilization (CCU) technologies, hydrogenation of CO_2 represents a strategic solution for the conversion and valorization of a greenhouse gas with the production of a clean fuel. In this study, a series of CuZnZr catalysts were prepared and their catalytic behavior was investigated in the hydrogenation of CO_2 to MeOH by changing the conditions of pretreatment to study the effect of copper phase on the activity-selectivity pattern. Considering the debate regarding the reaction mechanism and the univocal identification of the active sites in Cu-based catalysts, operando spectroscopic studies have been exploited to determine reactivity of adsorbate species and nature of active sites, intermediate or transient products after different pre-treatment steps[1,2].

Materials and Methods

A series of $Cu\text{-}ZnOZrO_2$ catalysts at different atomic composition were prepared by the gel-oxalate co-precipitation method and calcined at 350°C. Analytical, morphological, structural and surface properties were investigated by using XRF, XRD, SEM and TEM microscopy, N_2 adsorption/desorption isotherm and Raman spectroscopy. *In operando* DRIFT-MS measurements were performed using an environmental chamber located inside IS50 Thermofisher Spectrometer hyphenated with a Mass Spectrometer. Catalyst testing under CO_2 hydrogenation conditions was carried out in the temperature range 200-260°C at a pressure of 3.0 MPa, using a semi-automatic laboratory plant equipped with an electronic control unit for thermoregulation and mass-flow controllers.

Results and Discussion

Previous work had already demonstrated that the gel-oxalate coprecipitation method result to be effective and reproducible[2], ensuring precise control over the structural and morphological properties of the catalysts, accounting for the formation of well-dispersed spherical nanometric particles. The catalysts were characterized by similar surface area values (~32 m^2/g) and a pore distribution within the mesopore range, with no contribution from microporosity, typical of oxide-based catalytic systems. XRD analysis allowed to investigate the crystalline structure of the materials, while Raman spectroscopy provided detailed insights into the distribution of CuO and ZnO crystalline species. Notably, zirconia was identified not only in its amorphous form but also as partially

crystallized in both tetragonal and monoclinic phases (Fig. 1A). The effect of reduction pretreatment on catalyst activation was assessed performing the CO_2 hydrogenation reaction upon different pretreatment protocols: 1) pre-reduction in H_2 flow; 2) CO/He flow; 3) no pretreatment. No significant differences in CO_2 conversion and MeOH selectivity were observed, suggesting that the feed composition ensures the formation of the active sites necessary for the reaction. XRD patterns and HRTEM images of *used* samples revealed the presence of crystalline metallic copper phases, regardless of the pretreatment applied, decorated by zinc oxides and zirconia (Fig. 1B).

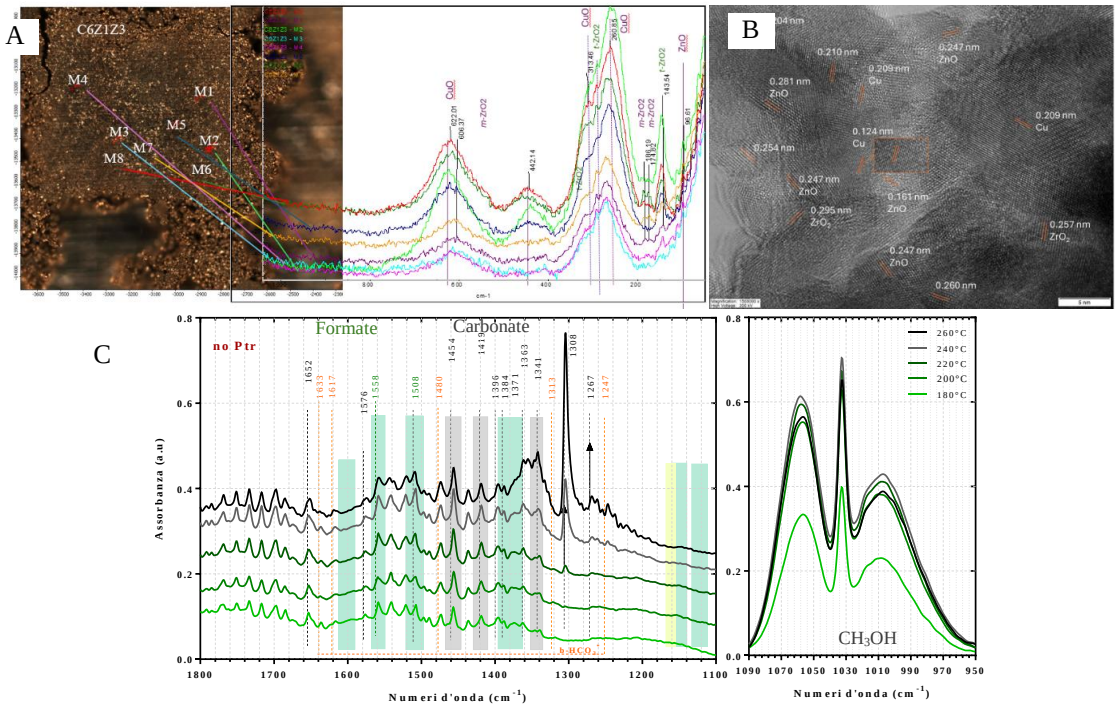


Figure 1 [A-B] Raman spectra and HR-TEM image of used $CuZnOZrO_2$ catalyst after CO_2 hydrogenation reaction without pre-reduction: [C] In operando DRIFT measurements during CO_2 hydrogenation without pre-reduction. T_R, 180-260°C; P_R, 30 bar; GHSV, 8,800 NL/kgcat/h; $CO_2/H_2/N_2$=3/9/1 mol/mol.

Based on the collected data during spectroscopic investigations in the DRIFT environmental cell, the competition among different reaction pathways was hypothesized depending on the adopted conditions. Specifically, formate species were confirmed as crucial intermediates in MeOH formation at lower temperature (<220°C), while at higher temperatures, the reverse water-gas shift reaction becomes dominant, leading to the formation of carbonate and bicarbonate species, via a mechanism involving CO as an intermediate. With no prereduction step, the formate pathway does not appear to be active at low temperature, as no adsorbed intermediate species were detected. Nevertheless, MeOH formation was observed at 180°C yet, alongside with CO adsorption on metallic copper sites. This highlights the reducing capability of the reaction mixture with time on stream, underscoring the critical role of the Cu^0/Cu^+ pair in both H_2 activation and stabilization of intermediate species.

References

1. J. Nyari, M. Magdeldin, M. Larmi, M Jarvinen, A. Santasalo-Aarnio, *J. CO_2 Utilization* **2020**,101166.
2. G. Bonura *et al*. *Appl. Catal. B* **2021,** 294, 120255-120264.

Acknowledgements

This research was funded by the EU – NextGeneration EU from the Italian Ministry of Environment and Energy Security POR H_2 AdP MMES/ENEA, Joint Agreement CNR-HAS 2023-2025 and the National Recovery and Resilience Plan, funded by the EU—NextGenerationEU - PNRR IR0000020, ECCSELLENT-Development of ECCSEL-R.I. Italian facilities: user access, services and long-term sustainability.

A Phoenix-like Covalent Triazine Framework as a Selective CO_2-to-Formate Electrocatalyst

Giuliano GIAMBASTIANI*[,1,2] Giulia TUCI,[2] Andrea ROSSIN,[2] Claudio EVANGELISTI,[3] Giovanni VALENTI,[4] Francesco PAOLUCCI,[4] Yuefeng LIU[5]

[1] *University of Florence, Dept. of Chemistry "U. Schiff" DICUS, Via della Lastruccia 13, Sesto Fiorentino, Italy.*
** giuliano.giambastiani@unifi.it*
[2] *Institute of Chemistry of OrganoMetallic Compounds, ICCOM-CNR and Consorzio INSTM, Via Madonna del Piano, 10 - 50019, Sesto Fiorentino, Florence, Italy.*
[3] *Institute of Chemistry of OrganoMetallic Compounds, ICCOM-CNR, Via G. Moruzzi 1 – 56124, Pisa, Italy.*
[4] *Department of Chemistry "Giacomo Ciamician", University of Bologna, 40126 Bologna, Italy.*
[5] *Dalian National Laboratory for Clean Energy (DNL), Dalian Institute of Chemical Physics, Chinese Academy of Science, 116023 Dalian, China.*

Significance and Relevance

We present the first example of an N-doped C-nanoarchitecture from the CTF series as a metal-free catalyst for the almost chemoselective electrochemical CO_2-to-HCOOH reduction (FE_{HCOOH} = 66%) already under moderate reducing potentials (− 0.4 V *vs*. RHE).

Preferred and 2nd choice for the topic: Catalysis to electrify the chemical production or CO_2 utilization and recycling

Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster) **Oral preferred or Short Oral or Poster**

Introduction and Motivations

The contribution unveils the silent electrochemical potentiality of a CTF sample already known as only moderately active in the CO_2-to-CO electroreduction.[1] As a modern *Phoenix*,[2] the mythological bird that regenerates from its own ashes, the CTF sample described demonstrates the impact that pyrolysis conditions have on the ultimate chemical, electronic, and morphological properties of these complex materials, giving rise to a robust catalyst with superior CO2RR selectivity toward the almost-exclusive formic acid production , at low overpotential values in an aqueous electrolyte (FE_{HCOOH} as high as 66% at − 0.4 V *vs*. RHE).

[1] Zhu, X.; Tian, C.; Wu, H.; He, Y.; He, L.; Wang, H.; Zhuang, X.; Liu, H.; Xia, C.; Dai, S. Pyrolyzed Triazine-Based Nanoporous Frameworks Enable Electrochemical CO2 Reduction in Water. *ACS Appl. Mater. Interfaces* **2018**, *10*, 43588-43594.
[2] Burton, M. The myth of the Phoenix. *J. R. Soc. Arts* **1961**, *109*, 382-386.

Materials and Methods

The CTF sample of the study was prepared under classical ionothermal conditions according to literature procedures. In brief, 1,3-dicyanobenzene (mDCB) was mixed in a dry-box with an excess of anhydrous $ZnCl_2$ (5 eq.) and transferred in a quartz ampule. After drying under vacuum for 3 h, the ampule was flame-sealed and heated in a furnace (10 h at 400 °C + 10 h at 600 °C). After cooling down to r.t., the ampule was carefully opened (caution: the ampule is under pressure) and the recovered black monolith crushed and submitted to sequential washing cycles (water, HCl 1M, NaOH 1M, water and THF) before being dried to constant weight (91 % yield).

Results and Discussion

We present a rare example of an N-doped C-nanoarchitecture from the CTF series as a metal-free catalyst for the almost chemoselective electrochemical CO_2-to-HCOOH reduction already under moderate reducing potentials (−0.4 V vs. RHE), corresponding to a faradic efficiency (FE_{HCOOH}) as high as 66% (**Figure 1**). The study highlights the impact of ionothermal conditions on the electronic and

morphological properties of the final CTF sample. As a modern "Phoenix", the pyrolyzed CTF described in this contribution regenerates from its ashes and transforms what is generally recognized as a moderately active CO_2-to-CO electrocatalyst in a unique and robust CTF with superior CO2RR selectivity toward the challenging CO_2-to-HCOOH electroreduction. In contrast with the general perception of pyrolysis for nanocarbon synthesis as highly batch-dependent procedures, the described protocol has unveiled an exceptionally high extent of reproducibility in terms of CTF electrochemical performance. Although any conclusion on the role of doping and material morphology, with respect to the prevalent CO_2-to-HCOOH 2e$^-$ reduction path, remains speculative, it can be postulated that the presence of a high density of "chemically accessible" basic sites favors the generation of a positive CO_2 concentration gradient at the catalyst surface. At the same time, electron-poor C-sites ($C^{\delta+}$) neighboring heteroelements foster an end-on activation of CO_2 molecules through their more electron-rich oxygen atoms ($O^{\delta-}$). Thus, CO_2 undergoes a first proton-electron transfer with the generation and stabilization of the *OCHO species as the formic acid precursor.[1]

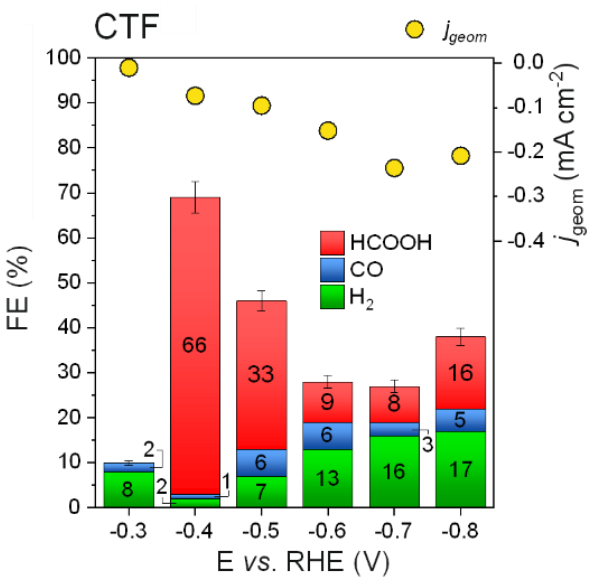


Figure 1. Faradaic Efficiency (FE_{HCOOH} - red, FE_{CO} - blue, FE_{H2} - green) and total (jgeom - yellow dots) current density values measured for the plain (metal-free) CTF in the -0.3 ÷ -0.8 V potential range vs. RHE.

The metal-free electrocatalyst doping with a Nickel active phase in the form of small-sized Ni^0@$Ni^{2+/3+}$ core-shell-like nanoparticles (NPs) leads to speculation on the synergistic or exclusive action of the two potentially active species in CO2RR (N-doped C-network *vs.* Ni NPs). The role of nickel species in promoting the CO_2-to-HCOOH electroreduction (where the plain CTF carrier failed) has also been unveiled.[2] The comparative study will also be discussed.

References

1. M. Moro, G. Tuci, A. Rossin, C. Salvatici, E. Verlato, C. Evangelisti, F. Paolucci, G. Valenti, Y. Liu, and G. Giambastiani, *ACS Materials Lett.* **2024**, 6, 583-589.
2. G. Tuci, M. Moro, A. Rossin, C. Evangelisti, L. Poggini, M. Etzi, E. Verlato, F. Paolucci, Y. Liu, G. Valenti and G. Giambastiani, *Nanoscale*, *asap*

Acknowledgements

The Italian MUR through the PRIN2022 project "MATISSE - A "Molecular Lift" for the Control of the Metal Protrusion and Coordination Sphere in Single-Atom Catalysts for CO2 Electroreduction" (2022K5SX27) and the European Union – NextGeneration EU through the Italian Ministry of Environment and Energy Security POR H2 AdP MMES/ENEA with involvement of CNR and RSE, PNRR - Mission 2, Component 2, Investment 3.5 "Ricerca e sviluppo sull'idrogeno", (B93C22000630006) are kindly acknowledged for financial support. G.G. and Y.L. also thank the CAS President's International Fellowship Initiative (PIFI) program for support to this research activity.

Atomic-scale insights into nanostructured MgO for thermocatalytic CO_2-to-CO conversion

Hsin-Yu Chen[1,2], Shih-Yuan Chen*[3], Cheng-Hsi Yeh[2], Chien-Neng Liao[1,4], and Hsin-Yi Tiffany Chen*[1,2,4]

[1]*National Tsing Hua University, Department of Materials Science and Engineering, Hsinchu 300044, Taiwan.*
[2]*National Tsing Hua University, Department of Engineering and Systems Science, Hsinchu 300044, Taiwan.*
[3]*National Institute of Advanced Industrial Science and Technology (AIST), Energy Catalyst Technology Group, Energy Process Research Institute (EPRI), 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan.*
[4]*College of Semiconductor Research, National Tsing Hua University, Hsinchu 300044, Taiwan.*
*sy-chen@aist.go.jp (S.Y. Chen), hsinyi.tiffany.chen@gapp.nthu.edu.tw (H.-Y. T. Chen)

Significance and Relevance

Recently, global temperatures have risen by 1.5°C above pre-industrial levels, largely due to increased CO_2 in the atmosphere from burning fossil fuels, highlighting the need for CO_2 capture and conversion into high-value products as a key strategy for mitigating climate change and achieving a carbon-cycling society. This study reported a metal-free, thermocatalytic CO_2-to-CO conversion using nanostructured MgO(111), which, with its polar surface and terminal oxygen species, was active in converting CO_2 to CO at 450–500 °C, whereas conventional MgO(100) was not.

Preferred and 2nd choice for the topic: Sustainable and clean energy production and transport, CO_2 utilization and recycling
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The global temperature has risen by 1.5°C above pre-industrial levels by 2024, surpassing the Paris Agreement target. This increase is largely attributed to the rapid rise in atmospheric CO_2 from burning fossil fuels, significantly impacting our environment and increasing vulnerability to climate change. To combat this, capturing and converting CO_2 into high-value products has emerged as a promising solution, using dual-functional materials with basic sites for capture and metallic sites for conversion[1]. These processes are vital for mitigating global warming, advancing a low-carbon society, and improving quality of life for future generations. However, Earth's limited metal resources are increasingly strained by rising demand for semiconductor-related applications essential to modern society. This study focused on a metal-free process for thermocatalytic CO_2-to-CO conversion, utilizing nanostructured MgO materials with either (111) or (100) facets. The structural properties of nanostructured MgO enriched with (111) facets (termed MgO(111)) and commercial MgO with (100) facets (termed MgO(100)) were systematically studied using atomic-scale microscopy, spectroscopy, temperature-programmed methods, and computational analysis. The results demonstrated that "metal-free" MgO(111), with its polar surface and terminal oxygen species, exhibited activity for the thermocatalytic conversion of CO_2 to CO—a key syngas component—at 450–500 °C, whereas MgO(100) did not.

Materials and Methods

MgO(111) was synthesized using a modified method[2]. $Mg(NO_3)_2$ was reacted with Na_2CO_3 to form white precipitates, which were washed with deionized water and ethanol, filtered, and calcined at 500–900 °C for 2 hours to produce nanostructured MgO(111). Commercial MgO(100) (99.9%, Wako) was used as a reference. The morphology and atomic structure of MgO(111) and MgO(100) were characterized by high-resolution transmission electron microscopy (HRTEM) with electron diffraction patterns (DP) and dark-field scanning transmission electron microscopy (DF-STEM). Their CO_2 capture and conversion capabilities were studied using in situ diffuse reflectance infrared Fourier transform spectroscopy and breakthrough curve analysis monitored by mass spectrometry (MS).

Results and Discussion

Figs. 1(a) and (c) present the HRTEM image with DP and DF-STEM image of MgO(111), respectively, compared to commercial MgO(100) as shown in **Figs. 1(b) and (d)**. The synthesized MgO(111) shows a

nanosheet-like, single-crystal morphology with a 0.15 nm lattice fringe, corresponding to the exposed {111} surface and a {220} facet along the <111> viewing direction. In contrast, commercial MgO(100) exhibits a larger crystal size with a (100) facet structure. Breakthrough curve analysis was conducted to examine the CO2 adsorption and desorption behavior of prepared MgO(111) using a Belcat II instrument with an MS detector (**Figs. 1(e)**, **1(f)**, and **Table 1**). The curve illustrates CO_2 adsorption at 50 °C (light green area), representing total CO_2 uptake, and desorption under Ar flow at 50 °C (light yellow area) and 50–800 °C (light red area) during temperature-programmed desorption (TPD), corresponding to the release of physically and chemically adsorbed species, respectively. MgO(111) exhibits a high total CO_2 uptake of 1.40 mmol g^{-1}, including a small amount of physically adsorbed CO_2 and a large amount of chemically adsorbed CO_2. Notably, a considerable number of CO is produced during the TPD process of CO_2, indicating that the thermocatalytic conversion of CO_2 to CO can be catalyzed by "metal-free" MgO(111). In contrast, MgO(100) shows minimal uptake of physically adsorbed CO_2, and neither CO_2 nor CO is observed during TPD. These results clearly demonstrate that MgO(111) effectively captures CO_2 and converts it into CO, whereas MgO(100) does not.

Table 1. Breakthrough curve analysis of CO_2 adsorption and desorption on nanostructured MgO(111) compared to commercial MgO(100).

Material	Total CO_2 uptake at 50 °C (mmol g^{-1})	Physisorption (%)	Chemisorption (%)	CO/CO_2[a] (%)
MgO(111)	1.40	4.0	96	10
MgO(100)	0.11	100	0	0

a. Quantitative analysis of CO and CO_2 species at TPD region.

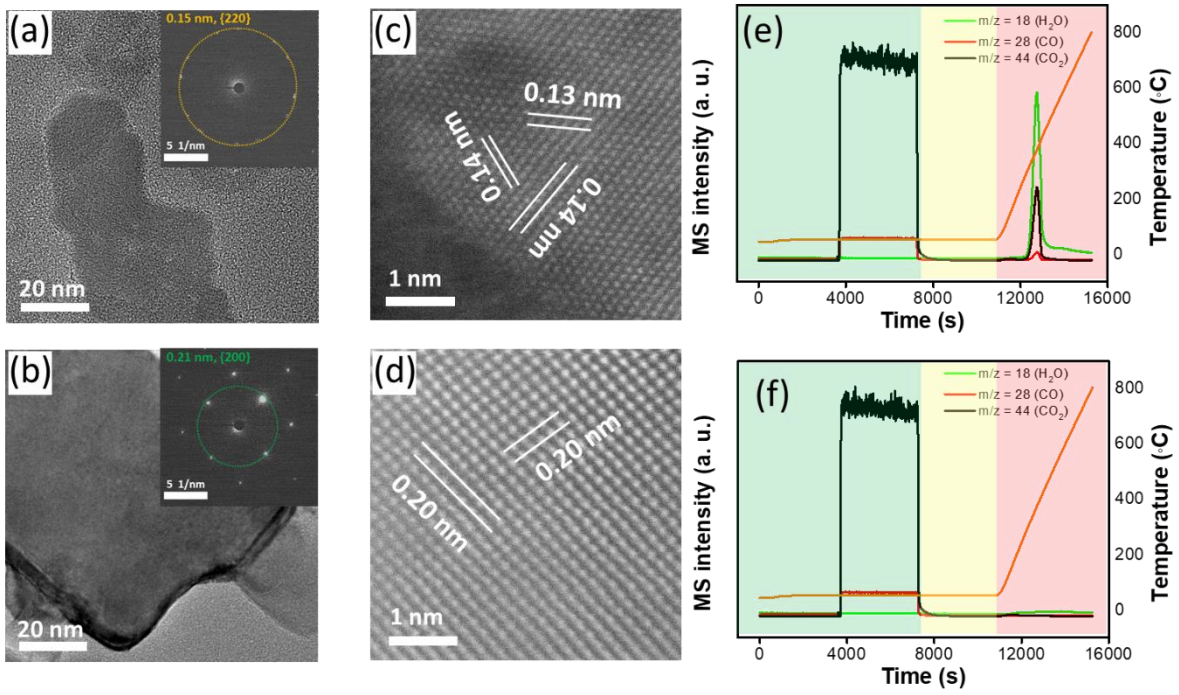


Figure 1 HRTEM images, diffraction patterns, DF-STEM images and breakthrough spectra (a, c, e) MgO(111) and (b, d, f) MgO(100).

References

1. F. Kosaka *et al.*, *ACS Sustain. Chem. Eng.* **2021,** 9, 3452-3463.
2. P. Liu *et al.*, *Angew. Chem. Int. Ed.* **2021,** 6, 3254-3260.

Acknowledgements

S.Y. Chen would like to thank AIST, Japan, and H.-Y.T. Chen would like to thank the National Science and Technology Council and National Tsing Hua University, Taiwan, for their financial support.

Enhanced CO_2 Hydrogenation to Hydrocarbons via SIL-Modified Fe-Ru/Al_2O_3 Catalysts: Tailoring Activity and Selectivity Through Support Engineering

Juan José Villora-Picó[1], Marina Maddaloni[2], Ander Centeno-Pedrazo[1], Jillian Thompson[1], Chunfei Wu[1], Nancy Artioli[2,*], and Haresh Manyar[1,*]

[1]*School of Chemistry and Chemical Engineering, Queen's University Belfast, David-Keir Building, Stranmillis Road, Belfast, BT9 5AG, UK;*

[2]*CEEP Laboratory, Department of Civil Engineering, Architecture, Territory, Environment and Mathematics, University of Brescia, via Branze 38, 25123 Brescia, Italy.*

Email: h.manyar@qub.ac.uk, nancy.artioli@unibs.it

Significance and Relevance

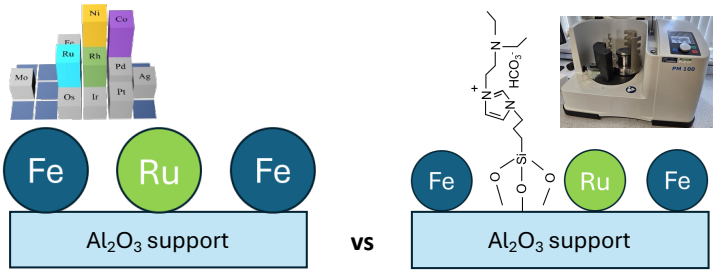
This study highlights the significance of modifying Al_2O_3 supports with supported ionic liquids (SILs) to enhance the catalytic performance of Fe-Ru-based catalysts for CO_2 hydrogenation to produce short-chain hydrocarbons when compared to the conventional colloidal synthesis approach. This work marks a significant advancement in the field, with the potential to contribute to sustainable energy solutions such as converting CO_2 into net-zero e-fuels for transportation and using CO_2 as a carbon feedstock for renewable resource development. The incorporation of SILs improves bimetallic interactions, reducibility, and particle size control, leading to increased CO_2 conversion and tunable product selectivity. Notably, SIL-modified catalysts exhibit a shift in selectivity trends, enabling the production of methane or higher hydrocarbons depending on metal loading.

Introduction and Motivations

The direct conversion of carbon dioxide into lower olefins (C2-C4) is a highly desirable process as a sustainable production route. These lower olefins, such as ethylene, propylene, and butenes, are crucial components in the chemical industry and for Liquefied Petroleum Gas (LPG). The production of hydrocarbons from CO_2 and H_2 is a promising strategy to mitigate CO_2 emissions. While noble metals have traditionally been used as catalysts, their high cost and limited availability have led to the exploration of non-noble metals, such as Ni and Fe, which show potential due to their cost-effectiveness. However, their stability is limited by coke deposition and metal sintering. The addition of small amounts of noble metals as promoters has proven effective in mitigating deactivation and enhancing selectivity toward higher hydrocarbons (C_2^+).[1] Catalytic performance is also highly sensitive to particle size and metal-metal interactions. The incorporation of ionic liquids (ILs) onto the catalyst support surface, forming Supported Ionic Liquids (SILs), enables precise control over particle size.[2] This results in the formation of smaller nanoparticles and promotes enhanced interactions between the metallic phases, thereby improving catalytic activity and stability. Fe-Ru/Al_2O_3 bimetallic catalysts were synthesized and Al_2O_3 was modified by incorporating an imidazolium-derived SIL using a solvent-free methodology. The effects of this modification on the physicochemical properties of the catalysts were evaluated, as well as their impact on performance in the CO_2 hydrogenation reaction. Advanced characterizations and extensive tests reveal that this method surpasses traditional colloid-based techniques, resulting in superior selectivity for target hydrocarbons.

Materials and Methods

The Supported Ionic Liquid (SIL) was synthesized using SiO_2 as the base material, followed by its incorporation on Al_2O_3 support via ball milling (**Scheme 1.**). Fe-Ru/Al_2O_3 catalysts were prepared through wet impregnation using $FeCl_3$ and $RuCl_3$ as precursors. The preparation included *in situ* chemical reduction with $NaBH_4$,



Scheme 1. (a) bimetallic Fe-Ru/Al_2O_3, and **(b)** SIL-modified Fe-Ru/Al_2O_3

subsequent washing, drying, and calcination at 400 °C. The catalysts were characterized using various techniques such as N_2 physisorption, TPR, XRD, FTIR, TGA, and ICP-OES analyses.

Catalytic performance was evaluated in a continuous-flow stainless steel tubular reactor. Prior to testing, all samples were pre-reduced at 400 °C. The CO_2 hydrogenation reaction was conducted at 20 bar with a gas mixture of 24% CO_2, 72% H_2, and 4% N_2, with a gas hourly space velocity (GHSV) of 1800 mL/g·h within the temperature range of 240–400°C.

Results and Discussion

The reducibility of the catalysts was analysed via Temperature-Programmed Reduction (TPR) (**Figure 1a**). The TPR profiles reveal two reduction peaks at approximately 150 °C in all samples, which are attributed to the reduction of Ru species. For the catalysts prepared without IL, a broad reduction peak appears between 500–700 °C, corresponding to the reduction of Fe_2O_3 to Fe. In contrast, catalysts modified with SIL exhibit distinct behavior, showing two peaks: one peak between 250–300 °C and an additional peak at around 450 °C. These peaks are associated with the stepwise reduction of Fe_2O_3 to Fe_3O_4 and the reduction of Fe_3O_4 to Fe, respectively. These results suggest that the incorporation of SIL onto the Al_2O_3 support significantly enhances the interaction between Fe and Ru species promoting Fe reduction. This enhanced bimetallic interaction is advantageous for the CO_2 hydrogenation reaction, as it promotes the formation of hydrocarbons.

As shown in **Figure 1b** and **1c**, the catalytic performance results indicate that catalysts prepared without IL exhibit low activity for CO_2 hydrogenation with CO as the major product. However, a remarkable improvement in activity and significant shift in selectivity from CO to CH_4 and C_2-C_5 hydrocarbons is observed with the modification of Al_2O_3 with IL. The 1%wt. Al_2O_3 + IL sample showed 46% CO_2 conversion with a selectivity of 82% to CH_4 and around 8% C_2-C_5 hydrocarbons. These findings highlight the critical role of SIL and metal loading in modulating both activity and product distribution during CO_2 hydrogenation.

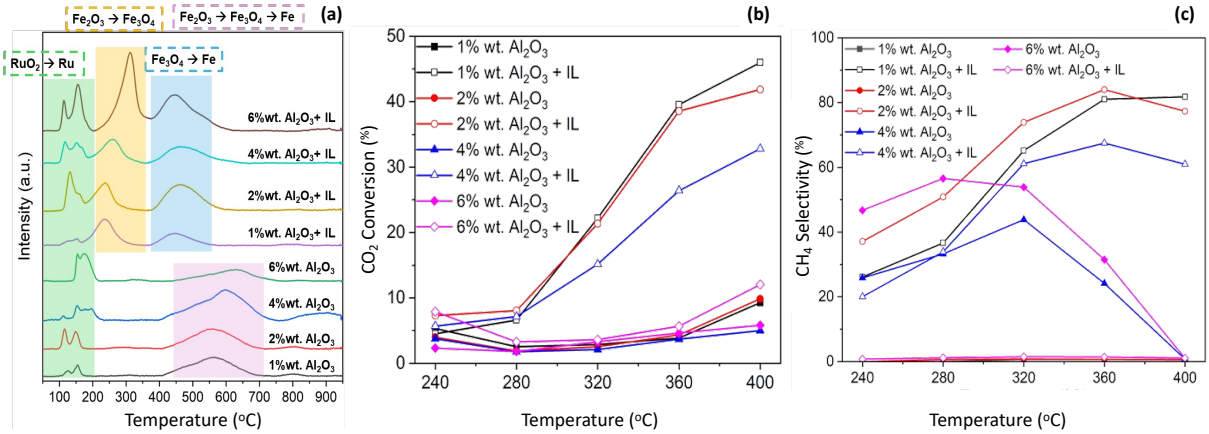


Figure 1. (a) TPR profiles (hydrogen consumption) of the prepared catalysts, Catalytic activity comparison of the samples: **(b)** CO_2 conversion, and **(c)** CH_4 selectivity respectively.

References

1. M. Maddaloni; A. Centeno-Pedrazo; S. Avanzi; N. J. Mazumdar; H. Manyar; N. Artioli, Catalysts **2023**, *13*, 1499.
2. N. Kusumawati; T. Sasaki; M. Shirai; ACS Appl. Nano Mater. **2023**, *6*, 17913-17923.

Acknowledgements

The authors gratefully acknowledge the financial support from Centre for Advanced Sustainable Energy (CASE) through the Green Innovation Challenge Fund for the project, “Integrated Capture and Conversion of CO_2 to Emission Free Fuels”. H.M. also thankfully acknowledges the funding and support provided by the Leverhulme Trust research grant RPG-2020-301, as well as the UK Catalysis hub via our membership of the UK Catalysis Hub Consortium funded by EPSRC grant: EP/R026645/1.

Effect of pre-treatment conditions on Fe-based catalyst for e-fuel production via modified Fischer-Tropsch synthesis

Alessio TAURO[1], Fabio SALOMONE[1], Fabrizio CELORIA[1], Marco ARMANDI[1], Luca NODARI[2], Luca ROMAGNOLETTI[3], Emanuele FELLI[4], Raffaele PIRONE[1], Samir BENSAID[1,*]

[1] *Polytechnic of Turin, Dept. of Applied Science and Technology, Corso Duca degli Abruzzi 24, 10129 Turin, Italy.*
[2] *Istituto di Chimica della Materia Condensata e di Tecnologie per l'Energia (ICMATE), Consiglio Nazionale delle Ricerche (CNR), C.so Stati Uniti 4, 35127 Padova, Italy.*
[3] *API Raffineria di Ancona S.p.A., Via Flaminia 685, 60015 Falconara Marittima (AN), Italy.*
[4] *Italiana Petroli S.p.A., Via Salaria 1322, 00138 Roma, Italy.*
* samir.bensaid@polito.it

Significance and Relevance

This work is significant for advancing CO_2-modified Fischer-Tropsch synthesis (FTS) by demonstrating how tailored pre-treatment conditions affect catalyst phase composition and performance. By integrating Na-Fe_3O_4 with controlled carburization techniques, the study highlights the formation of specific iron carbides, notably ε'-$Fe_{2.2}C$, which enhance hydrocarbon yield and selectivity toward long-chain products. The use of Mössbauer spectroscopy, DHA, and chemometrics provides a comprehensive analysis of phase transformations and product distributions. These insights are critical for optimizing catalysts in CO_2-to-fuel conversion processes, paving the way for sustainable and efficient fuel production.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling / Sustainable and clean energy production and transport.
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The rising demand for sustainable fuels has driven advancements in CO_2 conversion technologies, particularly in Fischer-Tropsch synthesis (FTS) for producing liquid hydrocarbons. This study examines the effects of various pre-treatment conditions on a Na-Fe_3O_4 catalyst in CO_2-modified FTS[1], focusing on how iron carbide formation influences hydrocarbon yield and distribution. By exploring how different pre-treatment strategies impact catalyst efficiency and selectivity, this research provides valuable insights into optimizing the CO_2-to-hydrocarbon conversion pathway.

Materials and Methods

The Na-Fe_3O_4 catalyst was synthesized via a precipitation method, followed by a series of pre-treatment conditions, including activation and carburization at varying temperatures and gas atmospheres, to promote specific iron carbide phases: H_2 activation at 450°C (pretreatment A); H_2 activation at 450°C followed by carburization (CO/H_2 1:1 P=2 bar) at 300°C (AC) and at 400°C (AC400).

The activity of the catalysts was tested between 320°C and 380°C, $H_2/CO_2/N_2$: 15/5/3, 7 NL/h/g_{cat}, 360 °C, 23 bar. Characterization techniques such as XRD, Mössbauer spectroscopy, and Detailed Hydrocarbon Analysis (DHA) were employed to evaluate the catalyst's bulk composition, surface properties, and resulting hydrocarbon distributions. Principal Component Analysis (PCA) was applied to DHA data to examine correlations between the hydrocarbon product distribution and the iron carbide phases of the catalyst, induced by the pretreatment and the specific reaction conditions (also replicating the composition of a feed deriving from the recirculation of primary unreacted or uncondensed species, i.e. mainly CO and CH_4).

Results and Discussion

The results reveal that pre-treatment conditions significantly influence the formation of active iron carbides **(Fig.1-right)**. Carburization at 400°C (AC400) proved optimal, promoting ε'-$Fe_{2.2}C$ formation

while minimizing α-Fe content, an inactive site for the reaction. The high-temperature carburization (400°C) an improved yield of C_5^+ hydrocarbons **(Fig.1-left)**, ranging from 14% to 18%, comprising a balanced light-to-heavy oil ratio, while A and AC lead to a predominance of light oil (T_{cond}<150°C) **(Fig.2)**. Although the Hagg Carbide (χ-Fe_5C_2) is the main phase often associated with CO_2 conversion activity, other carbides could play a role[2]: in this case, the presence of ε'-$Fe_{2.2}C$ enhanced the catalyst's selectivity for long-chain hydrocarbons, resulting in a diverse hydrocarbon distribution dominated by iso-paraffins, while shorter-chain olefins were predominant in other pre-treatment samples with lower or no ε'-$Fe_{2.2}C$ content. The combined use of Mössbauer, DHA, and chemometric analysis proved instrumental in identifying active carbide phases and understanding their impact on reaction pathways. These insights contribute to the development of tailored catalytic processes for CO_2-to-fuel conversion, highlighting the potential of optimized Na-Fe_3O_4 catalysts for sustainable fuel production.

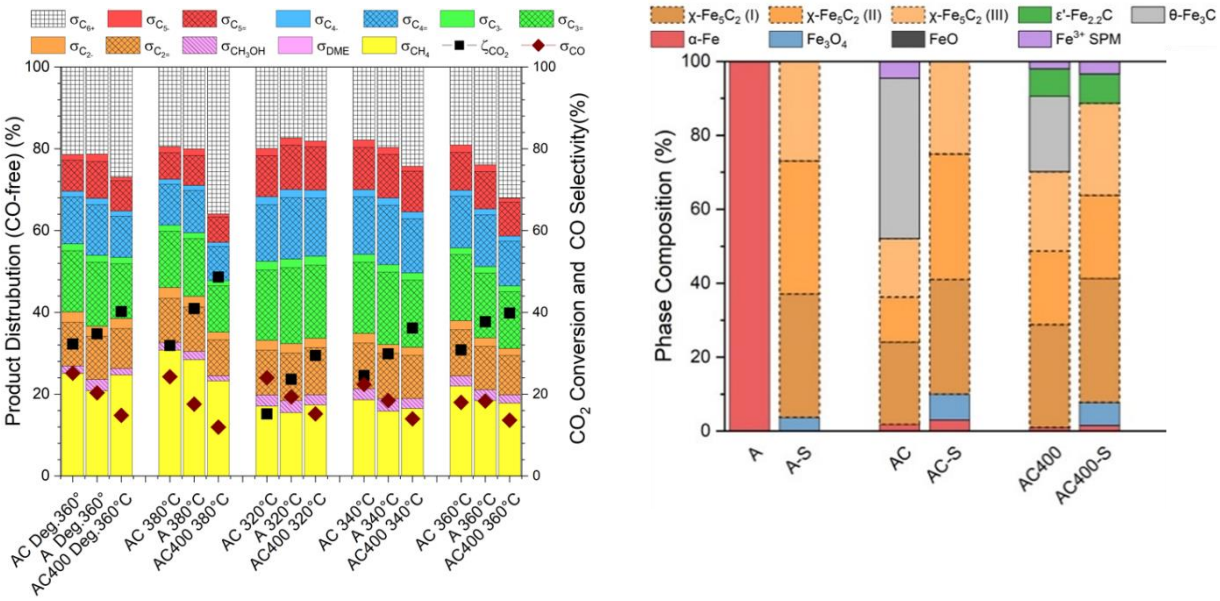


Figure 1 CO_2 conversion and product selectivity at different reaction temperatures (left); phases distribution in fresh and spent (S) samples tested at 360°C (right).

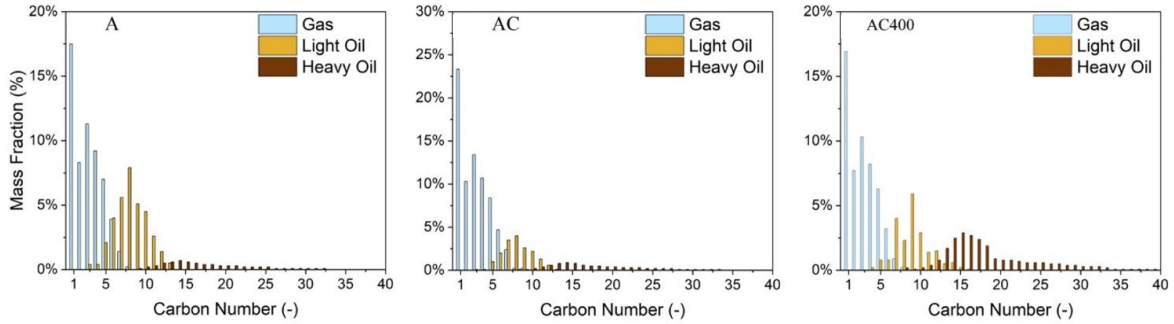


Figure 2 Product distribution subdivided by gaseous, light oil (T_b<150°C) and heavy oil (T_b>150°C).

References

1. M. V. Landau, N. Meiri, et al., Ind Eng Chem Res **2017**, vol. 56, no. 45, pp. 13334–13355
2. F. Lu, X. Chen, et al., Appl Catal B **2021**, vol. 281, p. 119521

Acknowledgements

The authors acknowledge the project PON Ricerca e Innovazione "REACT-EU" (DM 1062/21) funded by the Italian MUR and the PNRR program (DM 352/22) of the "Next Generation EU" program of the EU. Thanks to the Department of Chemical Sciences of Università di Padova for the Mössbauer analysis. Thanks to the API Raffineria di Ancona, Falconcara Marittima (Ancona) for the liquid samples analysis.

Improving Nickel Catalyst Dispersion on Phenol Hydrodeoxygenation by Amine-Assisted Impregnation

Claudio Contreras-Díaz[1,2]*, Cesar Pazo-Carballo[3], Claudio Araya-Lopez[1,2], C. Sepulveda[4] and Néstor Escalona[1,2,3]**

[1]Pontificia Universidad Católica de Chile, Departamento de Ingeniería Química y Bioprocesos, Escuela de Ingeniería, Santiago, Chile.
[2]Núcleo Milenio en Procesos Catalíticos hacia la Química Sustentable, Santiago, Chile.
[3]Pontificia Universidad Católica de Chile, Departamento de Química Física, Facultad de Química y Farmacia, Santiago, Chile.
[4]Universidad de Concepción, Facultad de Ciencias Químicas, Edmundo Larenas 129, Concepción, Chile.
* cicontreras6@uc.cl;** neescalona@ing.puc.cl

Significance and Relevance

This work explores nitrogen-chelating agents to enhance nickel dispersion on support surfaces further. Obtaining a 70% dispersion of Nickel as active phase in SiO_2 changing the product distribution over phenol hydrodeoxygenation, this study may be applicable in all transition metal to improve their dispersion with an affordable treatment.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion(preferred), Sustainable and clean energy production and transport (2nd choice)
Preferred presentation: Poster

Introduction and Motivations

Catalytic reactions occur on the metal surface, making dispersion and surface properties key for catalyst activity and selectivity. Common methods for preparing Ni-supported catalysts include incipient wetness impregnation, ion exchange, and precipitation-deposition. Nickel nitrate is often preferred for its solubility and low decomposition temperature, though it can lead to metal agglomeration on high-surface-area supports [1].

To improve metal dispersion, sacrificial transition metal complexes have been used in impregnation methods [5], with chelating agents like citric acid [2], ethylenediamine [3], and EDTA [4]. Recent studies, such as Gao *et al.* [5], show that Ni-amine complexes yield high dispersion and small Ni particles.

Materials and Methods

Ni/SiO_2 catalysts with amines of different N numbers were prepared via incipient wetness impregnation with a 10 wt% nickel loading. $Ni(NO_3)_2{\cdot}6H_2O$ was dissolved in water with various chelating agents—NH_3, ethylenediamine (en), diethylenetriamine (DETA), and pentaethylenehexamine (PEHA)—at amine/Ni molar ratios of 6, 3, 2, and 1, respectively, to form $Ni(NH_3)_6$, $Ni(en)_3$, $Ni(DETA)_2$, and Ni(PEHA) complexes. After aging at room temperature and drying at 90°C, the precursors were calcined at 550°C for 2 h and labeled Ni/SiO_2, $Ni(NH_3)/SiO_2$, $Ni(en)/SiO_2$, $Ni(DETA)/SiO_2$, and $Ni(PEHA)/SiO_2$. Catalytic stability was evaluated in the vapor phase at 250°C using a fixed-bed quartz U-tube reactor. All catalysts were reduced in situ with H_2 (60 mL/min, 550°C) before introducing phenol into the reactor via an H_2 flow through a saturator at 100°C. Products were analyzed using a Nexis 2030 gas chromatograph.

Results and Discussion

Catalysts active phase dispersion, particle diameter and surface area are displayed in Table 1. It is observed a marked improvement in the dispersion of the nickel particles with the used of Ni-Amine clomplexes as a sacrificial agent. It is worth noting that the most dispersed active phase was found to be the Ni(PEHA) complex with a 70% dispersion and a 1.44 nm particle size obtained by CO-chemisorption and correlated with the particle size distribution of TEM. Besides, figure 1 is observed the difference of the selectivity distribution between Ni/SiO_2 and $Ni(PEHA)/SiO_2$ which could be related to the dispersion of the active phase.

Table 1: catalysts surface area, particle diameter obtained by TEM and CO-Chemisorption and dispersion

Catalysts	S_{BET} (m^2/g)	dp_{TEM}(nm)	dp_{CO}(nm)	Ni (%) Dispersion
SiO_2	347	-	-	-
Ni/SiO_2	285	9.89	14.79	7
$Ni(NH_3)_6/SiO_2$	383	1.97	1.56	64
$Ni(en)_3/SiO_2$	368	2.95	1.72	59
$Ni(PEHA)/SiO_2$	292	1.60	1.44	70

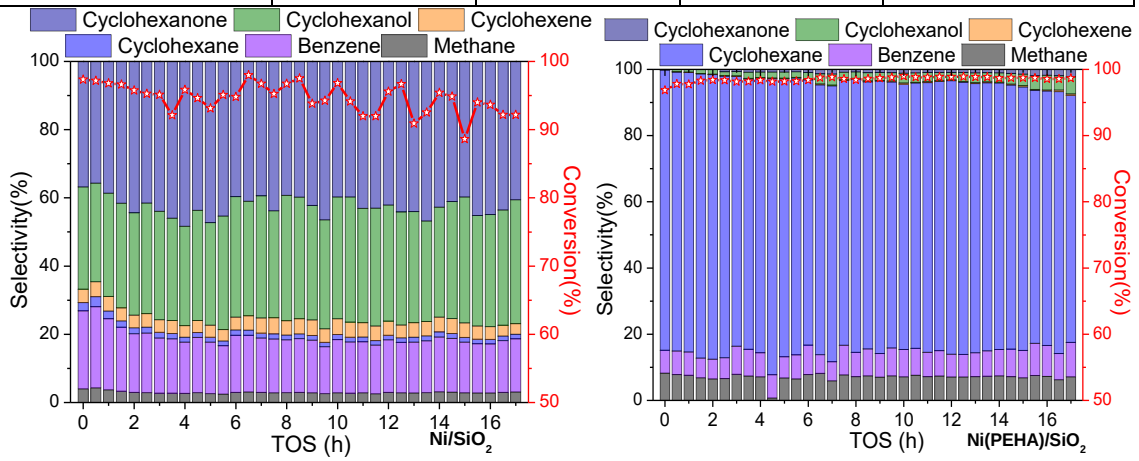


Figure 1 conversion and selectivity fixed-bed hydrodeoxygenation of phenol

References

1. S. Wang and G. Q. Lu, *Applied Catalysis A General*, **1998,** 169, 271–280
2. X. Li *et al.*, *Applied Catalysis A General*, **2024**, 671, 119564
3. S. Schimpf, C. Louis, and P. Claus, *Applied Catalysis A General*, **2007**, 318, 45–53
4. R. A. Ortega-Domínguez, H. Vargas-Villagrán, C. Peñaloza-Orta, K. Saavedra-Rubio, X. Bokhimi, and T. E. Klimova, **2017,** *Fuel*, 198, 110–122
5. X. Y. Gao, J. Ashok, S. Widjaja, K. Hidajat, and S. Kawi, *Applied Catalysis A General*, **2015**, 503, 34–42

Acknowledgements

This research was funded by the following sources: Fondequip No. EQM160070, The Millennium Science Initiative Program-NCN2021_090, FONDECYT regular (Grant No. 1220763), FONDEF ID23I10149, ANID ACT240050; C.C.D. was funded by Agencia Nacional de Investigacion y Desarrollo (ANID), Chile through doctoral grant 2021-(grant No. 21211077); and C.A.L. was funded by ANID, Chile, through FONDECYT Postdoctoral (Project3220395).

Tuning Multifunctionality for the Co-production of H_2, Carboxylic Acids and Electricity in a Multi-purpose Biomass-Fuel Cell

Bezawit Z. Desalegn, and Jeong Gil Seo*
Hanyang University, Department of Chemical Engineering, 04763, Seoul, South Korea.
Hanyang University, Clean-Energy Research Institute, 04763, Seoul, South Korea.
* jgseo@hanyang.ac.kr

Significance and Relevance

The simultaneous production of both carboxylic acids and H_2 gas at the anode via an ultra-low voltage aldehyde oxidation was realized over a bimetallic CuNi alloy. The synergistic interaction between metallic Cu and Ni sites is found to be the dominant factor in controlling the production of H_2 and the cyclability of the electrodes with considerable carboxylic acid and H_2 production during consecutive cycles. Moreover, the importance of metallic sites in the activation of H* was confirmed thorough H_2 TPD analysis wherein, the absence of metallic sites resulted in weak to no interaction with H*.

Preferred and 2nd choice for the topic: *Sustainable and clean energy production and transport/* ***2nd choice****: Catalysis to electrify the chemical production*
Preferred presentation**:** *Oral preferred or short oral*

Introduction and Motivations

The development of economical and energy-efficient processes for the sustainable production of energy and green chemicals is fueled by the increasing concerns over exhausted petroleum resources, high oil prices, energy security and environmental concerns.[1] Hydrogen is a prospective clean fuel and a vital feedstock in industrial chemical processes. Despite the promise of water electrolysis as an alternative technology for producing high-purity H_2, the commercial scalability is limited by its high cost, due to the required high voltage input. While electrochemical biomass oxidation has been explored as an alternative anodic reaction for water electrolysis to produce cheap H_2, these conventional organic electrolyzer systems still require high voltage input (> 1V) resulting in high electricity consumption. Hence, the transformation of these energy input systems into an energy output system is of great significance. Unlike the conventional aldehyde electrooxidation, in which the hydrogen atom of the aldehyde group is oxidized into H_2O at high potentials, the ultralow-potential aldehyde oxidation enables the hydrogen atom to recombine into H_2 gas. [2] This H_2 generation from bio-based aldehydes can also be accompanied by the production of valuable by-products, such as carboxylic acids in the same anodic compartment. Cu is known to optimally balance the ability to activate the C-H bond, avoid CO poisoning and be stable in a metallic form at desired operating potentials.[3] Accordingly, in this work a CuNi alloy was constructed aiming to lower the barrier for C-H dissociation of the aldehyde group through the formation of diol-intermediates, while facilitating the adsorption of OH^- for the oxidation of furfural to furoic acid.

Materials and Methods

The self-supported Cubic CuNi alloys were synthesized via an electrodeposition method and directly used as anodes. The ultra-low potential aldehyde oxidation was performed by using furfural as a model aldehyde substrate in an H-type electrochemical cell separated by an AEM with a 1M KOH catholyte and 1M KOH + 400mM furfural anolyte. The simultaneous production of Furoic acid and H_2 at the anode was confirmed by high performance liquid chromatography (HPLC) and gas chromatography (GC) analysis.

Results and Discussion

The co-production of Furoic acid and H_2 gas at the anode was confirmed for the bimetallic CuNi alloys with the highest FA and H_2 production observed for 80%Cu and 20%Ni. Production of 0.7 mol FA and 0.16 mol H_2 was achieved per mole of furfural in just 30 mins of electrolysis at an applied voltage of 0.3V vs. RHE. The synergistic effect of metallic Ni and Cu was verified by the lack of H_2 production in the 1st cycle for electrodes with lower Ni% (<20%) content (**Figure 1**). For all the electrodes, an increased FA and H_2 production was observed after the 1st cycle which was accompanied by a decrease in (oxy)hydroxide peaks and an increase in the metallic Cu and Ni peaks which implies the in-situ reduction of (oxy)hydroxides to metallic active sites during the 1st cycle. These results suggest that metallic Cu/Ni sites to be the active sites for furfural activation/H_2 production which was confirmed by controlling the metallic composition by adjusting the synthesis parameters which increased H_2 production rate in the 1st cycle, followed by stable production of both H_2 and FA during successive cycles.

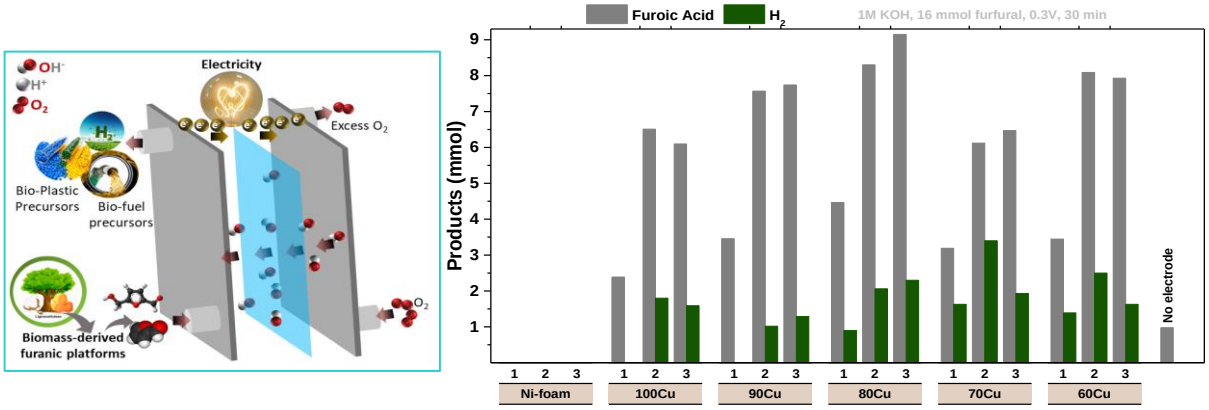


Figure 1. Schematic illustration of the proposed multipurpose biomass fuel cell (Left) and Effect of metal combination on the co-production of FA and H_2.

Accordingly, it is anticipated that due to the ultra-low applied voltage, the anodic furfural oxidation can be paired with cathodic ORR in a multi-purpose fuel cell to simultaneously produce H_2, FA and electricity advancing multifunctionality.

References

1. R. Mariscal, P. Maireles-Torres, M. Ojeda, I. Sádaba and M. López Granados, *Energy Environ. Sci.*, **2016**, **9**, 1144–1189.
2. T. Wang, L. Tao, X. Zhu, C. Chen, W. Chen, S. Du, Y. Zhou, B. Zhou, D. Wang, C. Xie, P. Long, W. Li, Y. Wang, R. Chen, Y. Zou, X. Z. Fu, Y. Li, X. Duan and S. Wang, *Nat. Catal.*, **2022**, **5**, 66–73.
3. H. Liu, N. Agrawal, A. Ganguly, Y. Chen, J. Lee, J. Yu, W. Huang, M. Mba Wright, M. J. Janik and W. Li, *Energy Environ. Sci.*, **2022**, **15**, 4175–4189.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (No. 2022R1I1A1A01064469).

Hydrogen release from perhydrobenzyltoluene: role of the catalyst support

Nataliia MARCHENKO, Mohamad KHARMA, Franck MORFIN, Laurent PICCOLO,
Nuno ROCHA BATALHA, Valérie MEILLE*
IRCELYON, CNRS, UCBL, 69100 Villeurbanne, France.
** valerie.meille@cnrs.fr*

Significance and Relevance

Perhydro-benzyltoluene (H12-BT) is one of the most popular LOHC. However, its dehydrogenation, to release pure hydrogen, generally produces trace amount of methylfluorene, which leads to coke formation after several cycles (dehydrogenation/hydrogenation). In this contribution, a new Pt/TiO_2 (rutile) catalyst was synthesized and showed a much lower methylfluorene yield during the dehydrogenation of H12-BT at 260°C.

Preferred and 2nd choice for the topic: H2 storage and transportation, green H2 production, hydrogen vectors / Sustainable and clean energy production and transport
Preferred presentation: Oral preferred or short oral

Introduction and Motivations

Among the different methods used to store hydrogen, either for transportation, mobility or intermittent usage, Liquid Organic Hydrogen Carriers seem to have a part to play. Based on the reversibility of the hydrogenation reaction, hydrogen can be stored and released depending on the operating conditions. The LOHC pair perhydrobenzyltoluene/benzyl-toluene (H12-BT/BT) is one of the most studied at the moment, because the molecules are cheap, easily available, and liquid in a wide range of temperature[1]. H12-BT stores 6.2wt-% of hydrogen. To recover hydrogen, a catalytic dehydrogenation is carried out, using platinum-based catalysts. In the present study, the support of Pt was studied, using the diversity of properties that titania can bring through its different phases. The objectives were 1) to have a catalyst at least as active as the standard Pt/Al_2O_3 and 2) to obtain a better selectivity to BT, avoiding the formation of methylfluorene as a side-product (Figure 1a).

Materials and Methods

The 0.5wt-%Pt/TiO_2 catalysts were prepared by the incipient wetness impregnation method followed by calcination and reduction treatments. Various anatase/rutile phase ratios were obtained starting from different commercial TiO_2 and using different thermal treatments. The resulting materials were named Pt/Ax, x being the percentage of anatase in the titania mixture.

The dehydrogenation reactions were carried out in a stirred glass semi-batch reactor, open to the gas (continuous removing of hydrogen), at a temperature of 260°C. The hydrogen productivity was obtained from the initial slope of H12-BT concentration vs. time (GC-FID analysis) and confirmed by the measurement of hydrogen flowrate (GC-TCD analysis).

Results and Discussion

All prepared 0.5wt-%Pt/TiO_2 powders showed average nanoparticle (NP) sizes from 1.0 to 1.4 nm. They were used in the catalytic dehydrogenation of H12-BT, at a Pt/H12-BT weight ratio of 0.009%. The materials presented different behaviors, confirmed by repeatable testing (Figure 1). The hydrogen productivity is shown in Figure 1b, Pt/A0 and various Pt/Ax (with x between 20 and 90) present higher performance than Pt/Al_2O_3. On the other hand, Pt/A100 and Pt/A15 are significantly worse. In Figure 1c, the methylfluorene yield was plotted vs. DoDH (degree of dehydrogenation). At 35% DoDH, methylfluorene reaches 0.35% for the commercial Pt/Al_2O_3 (99.0% selectivity), whereas it is less than 0.15% for Pt/A0 (> 99.5% selectivity). As methylfluorene is detrimental to the storage performance during repeated cycles[2], minimizing its production increases the durability of the system.

To explain the results, work is in progress to characterize the acidity of the different materials which could be the source of the side-product formation. It is indeed known that the titania surface acidity depends on the phase, rutile being much less acidic than anatase[3]. The structure sensitivity in the non-scalable Pt particle size regime is also explored using CO-IR spectroscopy. First results show that MF production might be a site-sensitive reaction.

To conclude, it was found that well-dispersed Pt nanoparticles supported on rutile are significantly more active than the Pt/Al_2O_3 reference and lead to much less methylfluorene by-product (-60%). Further work concerns the development of bimetallic Pt-M/rutile which may further help lower the Pt content.

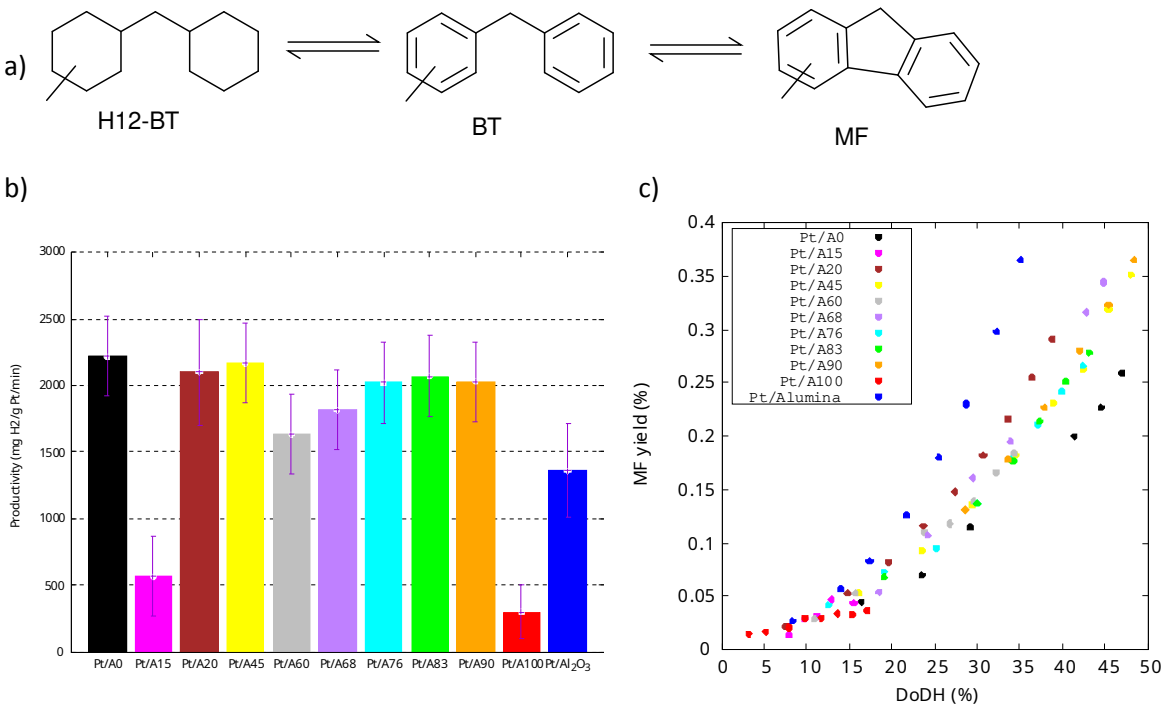


Figure 1 a) Dehydrogenation of H12-BT. b) Hydrogen productivity of various Pt/TiO_2 catalysts in comparison with Pt/Al_2O_3 during the H12-BT dehydrogenation at 260°C with a Pt/H12-BT ratio of 0.009wt-% - c) Methylfluorene yield as a function of the degree of dehydrogenation.

References

1. P. Modisha, D. Bessarabov, *Current Opinion in Green and Sustainable Chemistry* **2023**, 42, 100820
2. T. W. Kim, Y. Jo, K. Jeong, H. Yook, J. W. Han, J. H. Jang, G. B. Han, J. H. Park, Y.-W. Suh, *Journal of Energy Storage*, **2023,** 60, 106676
3. H. Li, M. Vrinat, G. Berhault, D. Li, H. Nie, P. Afanasiev, *Materials Research Bulletin*, **2013**, 48, 3374-3382

Acknowledgements

This work is a part of the UnLOHCked EU-HORIZON project funded by the Clean Hydrogen Partnership under Grant Agreement 101111964.

Overview of ZSM-5, CLI, and FAU catalysts with metallic dimers (Cu, Fe, Zn) and their sensitivity to poisoning by sulfur dioxide (SO_2) in the DeNOx process.

Izabela KURZYDYM*[1], Izabela CZEKAJ[2]
[1]*Faculty of Chemistry, Biological and Chemical Research Centre, University of Warsaw, ul. Żwirki i Wigury 101, 02-089 Warszaw, Poland*
[2]*Department of Organic Chemistry and Technology, Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 31-155 Cracow, Poland.*
** i.kurzydym@chem.uw.edu.pl*

Significance and Relevance

The study analyzes the impact of SO_2 present in the reaction mixture during the industrial deNOx process. Results indicate that SO_2 molecules adsorb onto the metal sites in dimeric structures within all investigated zeolites. This interaction demonstrates that SO_2 acts as a catalyst poison. Furthermore, the sensitivity to poisoning is strongly dependent on the type of catalyst. Among the tested zeolites, clinoptilolite exhibits the highest resistance to SO_2-induced deactivation.

Preferred and 2nd choice for the topic: Automotive and stationary emission control, Fundamental advances in understanding catalysis
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The emission of nitrogen oxides NOx has become the main problem among air pollutants emitted from various sources, such as automotive, energy and heavy industry. In addition, these oxides are a very serious problem both in terms of impact on human health and the environment cause for eg. acid rains and photochemical smog.[1] Currently, regulations require a significant reduction of these harmful oxides and the existing thresholds may be lowered again in the near future. The most effective way to dispose of nitrogen oxides to meet the required limits is the SCR deNOx reaction. Transition metal modified zeolites have recently gained the greatest interest among scientists.[2-4] The resistance of catalysts to sulfur oxide poisoning is also a critical factor in.[5] Actual exhaust gases typically contain 50–300 ppm SO_2. Selecting an appropriate support material is the most effective strategy for enhancing low-temperature catalytic activity and improving resistance to SO_2-induced deactivation.

Materials and Methods

The ab initio density functional theory (DFT) method was used to calculate the electron structure of the presented clusters with StoBe software. The exchange and correlation functional was approximated with a Perdew-Burke-Ernzerhof (PBE) functional. It was used for the electron exchange and correlation. Milliken populations and Mayer's bond order factors were used to precisely analyse the electron structure of the clusters.

Results and Discussion

The analysis presents an overview of the three zeolites: ZSM-5, FAU and clinoptilolite. Different variants of metallic dimers (CuOCu, CuOFe, CuOZn) were also selected. In addition, each dimer was presented in a partially hydrated form - an OH group on the bridging oxygen and an OH group on one of the metals (two variants for each dimer). This representation of the dimers is due to the presence of H_2O in the reaction mixture and the ability of the dimers to hydrate easily. The study showed that sulphur dioxide adsorbs onto the surface of the metal dimer in each of the three selected zeolites. The zeolite with the highest resistance to sulphur dioxide poisoning was found to be the clinoptilolite. This natural zeolite showed high efficiency in deNOx and deN_2O processes, and its resistance to poisoning confirms its validity for use in these processes.

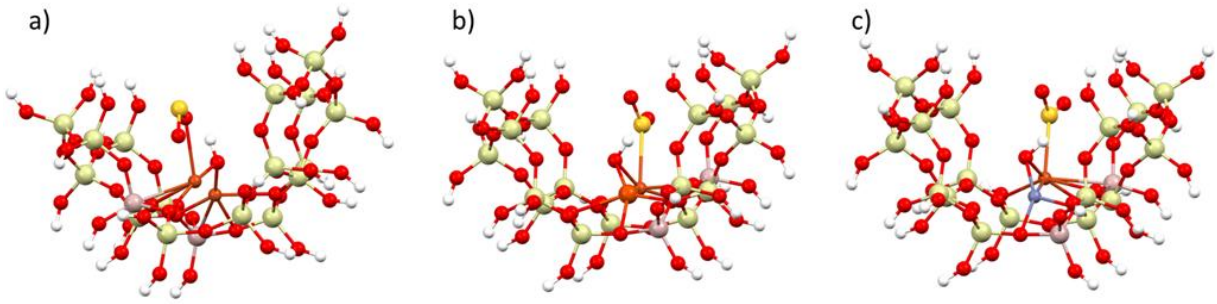


Figure 1. Structure of zeolite clinoptilolite ($Al_2Si_{16}O_{50}H_{28}$) with bimetallic dimers (a) Cu-OH-Cu (b) Cu-OH-Fe and (c) Cu-OH-Zn with adsorbed SO_2.

References

1. J. Bosch, F. Janssen, Catal. Today. 2, **1988**, 369–379.
2. T. J. Wang, S. W. Baek, H. J. Kwon, Y. J. Kim, I.-S. Nam, M.-S. Cha, G. K. Yeo, Ind. Eng. Chem. Res. 50, **2011**, 2850-2864.
3. I.Czekaj, S. Brandenberger, O. Kröcher, Micropor. Mesopor. Materials 169, **2013**, 97-102.
4. I.Kurzydym, I.Czekaj, Molecules 29(10), **2024**, 2329.
5. Q. Wang, C. Gu, Z. Jiang, Y. Lu, F. Liu, J. Zhi, H. Shi, Chem. Phys. Impact 5, **2022**, 100118.

Acknowledgements

We gratefully acknowledge Polish high-performance computing infrastructure PLGrid (HPC Center: ACK Cyfronet AGH) for providing computer facilities and support within computational grant no. PLG/2024/017609

Promoting the efficient oxidation of toluene via non-thermal plasma-assisted synthesis of supported cobalt oxide catalysts

Victor DEBOOS[1,2], Savita Kaliya Perumal VEERAPANDIAN[2], Eliane GHOSSEIN[1,2], Jean-Marc GIRAUDON[1], Rino MORENT[2], Nathalie DE GEYTER[2], Jean-François LAMONIER*[,1]

[1]*Unité de Catalyse et Chimie du Solide (UCCS), Univ. Lille, CNRS, Centrale Lille, Univ. Artois, 59000 Lille, France*

[2] *Unit Plasma Technology (RUPT), Department of Applied Physics Faculty of Engineering and Architecture, Ghent University, 9000 Ghent, Belgium*

**jean-francois.lamonier@univ-lille.fr*

Significance and Relevance

The study reveals that a carefully controlled sequential Dielectric Barrier Discharge (DBD) plasma treatment offers a promising alternative to traditional calcination methods for the preparation of highly effective supported Co_3O_4 catalysts. The findings suggest that DBD plasma treatment can enhance key catalytic properties, such as redox behavior and surface reactivity, making it a potentially more sustainable and effective strategy for producing supported transition metal catalysts with high activity and stability in Volatile Organic Compounds (VOCs) total oxidation.

Preferred and 2nd choice for the topic: "Air cleaning and combustion" and "Automotive and stationary emission control"
Preferred presentation: Oral preferred

Introduction and Motivations

Volatile organic compounds (VOCs), harmful pollutants of both natural and human origin, impact health and the environment. Total catalytic oxidation using cost-effective supported transition metal oxides (TMOs) offers an efficient method to convert these pollutants at low temperatures while minimizing secondary emissions. Calcination in air is the usual approach for the preparation of dried impregnated supported TMOs starting from a supported TM salt. However, calcination conditions can lead to adverse effects such as sintering, TM cations diffusion into the support, resulting in a decrease of catalytic activity. To meet this challenge, non-thermal plasma (NTP) offers a promising and attractive alternative to classical calcination. The potential of NTP has been already discussed in the literature in the preparation of efficient supported TM catalysts[1]. Indeed, the low thermal effect of NTP can lead to rapid particle nucleation, slow particle growth and a better interaction with the support. In particular, Non-thermal dielectric-barrier discharge (DBD) plasma has gained increasing attention over the past decade for the plasma decomposition of nitrate precursors[2], as it proves to be more reactive than conventional glow discharge. Inspired from these findings, the present work aims to study the possibility of using a non-thermal DBD plasma as an alternative route to conventional calcination for the preparation of κ-alumina pellet-supported Co_3O_4 (10 wt% Co) to be tested in toluene total oxidation.

Materials and Methods

The precursor of the silica doped κ-Alumina pellet-supported Co_3O_4 (Co:10 wt% ; Co/Al_2O_3-D) was prepared by aqueous wet impregnation using $Co(NO_3)_2.6H_2O$ (> 99%, Sigma Aldrich) and κ-Al_2O_3 alumina (Alfa Aesar, SSA: 25 $m^2.g^{-1}$, pellets) as support followed by a drying step at 80°C (12h). Part of the precursor was calcined at 300 °C for 5 h (Co/Al_2O_3-C). Another part was activated *in situ* at 120 °C in air and then submitted to a dry air DBD plasma treatment (8.0 kV) in a short operation time of 45 min including three NTP on/off sequences (25/10 min + 10/10 min + 10 min). The plasma modified catalyst was labelled Co/Al_2O_3-P. The DBD reactor and plasma set-up were reported previously[3]. Both catalysts were tested for the total oxidation of toluene (1000 ppm in air; GHSV: 30 $L.h^{-1}.g^{-1}$) using a set-up described elsewhere[4].

Results and Discussion

The cobalt content (10 wt%) was confirmed by Inductively Coupled Plasma analysis. The structural properties were investigated using X-ray diffraction (XRD), infrared spectroscopy, and Raman spectroscopy. These techniques collectively demonstrate the decomposition of cobalt salts into Co_3O_4 on the surface of silica-doped κ-Alumina pellet supports, both for the calcined and plasma-treated samples. The crystallite size of Co_3O_4 (from XRD data) in the plasma-treated sample is slightly smaller (25 nm) compared to that in the calcined sample (30 nm). The redox properties were assessed using H_2-Temperature Programmed Reduction (H_2-TPR) experiments. The H_2 consumption values (2.27 $mmol \cdot g^{-1}$ for both samples) indicate the formation of Co_3O_4 particles. Notably, the H_2 consumption profile for the plasma-treated sample occurs at a lower temperature compared to the profile for the calcined sample (Figure 1), highlighting the superior redox properties of the plasma-treated material.

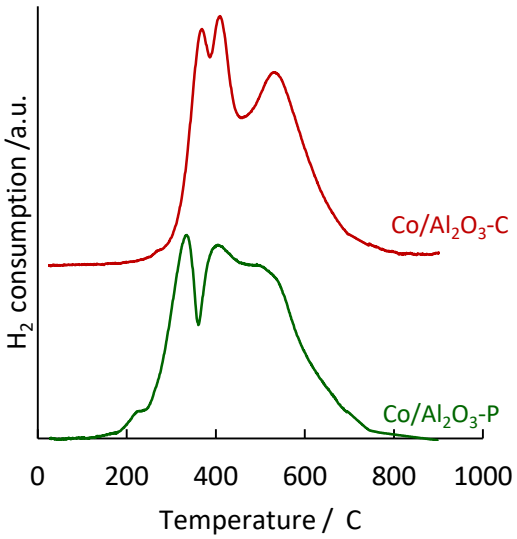


Figure 1 : H_2-TPR profiles of cobalt catalysts calcined or plasma treated.

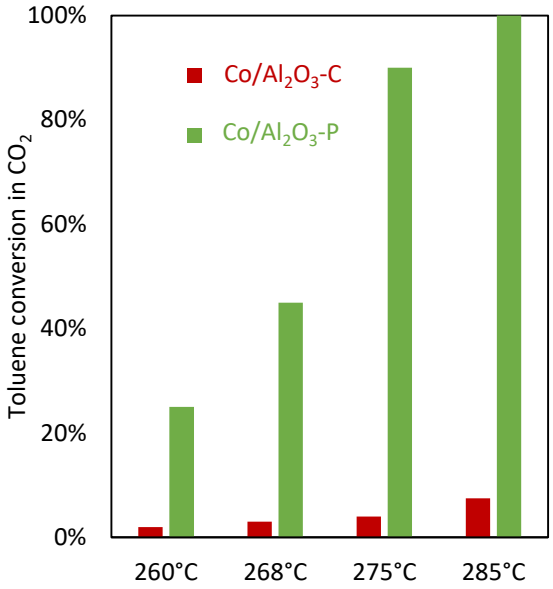


Figure 2 : Toluene total oxidation (1000 ppm toluene/air; GHSV: 30 $L.h^{-1}.g^{-1}$; -0.5 °C.min^{-1}).

The conversion of toluene to CO_2 as a function of temperature and catalyst type is illustrated in Figure 2. The results clearly indicate that the plasma-treated catalyst exhibits significantly higher activity than the calcined catalyst across the temperature range studied.

The improved catalytic performance of the plasma-treated sample can be attributed to the enhanced dispersion and redox properties of Co_3O_4, which contribute to more efficient toluene oxidation. These findings highlight the potential of plasma treatment in optimizing catalyst activity for environmental applications.

References

1. Z. Wang, Y. Zhang, E. C. Neyts, X. Cao, X. Zhang, B. W.-L. Jang and C. Liu, *ACS Catal.* **2018**, 8, 2093.
2. D C. Ye, T. Fang, X. Long, H. Wang, S. Chen and J. Zhou, *Environ. Sci. Pollut. Res.* **2022**, 30, 11994.
3. Z. Ye, S.K.P. Veerapandian, I. Onyshchenko, A. Nikiforov, N. De Geyter, J.-M. Giraudon, J.-F. Lamonier and R. Morent, *Ind. Eng. Chem. Res.* **2017**, 56, 10215.
4. Z. Ye, J.-M. Giraudon, N. Nuns, P. Simon, N. De Geyter, R. Morent, J.-F. Lamonier, *Appl. Catal. B* **2018**, 223, 154.

Acknowledgements

This research was supported and funded by the "DepollutAir" and "CleanAirBouw" projects, which are part of the European INTERREG France-Wallonie-Flanders FEDER program.

NOx emission control by H_2-SCR over Pt-ZSM5 catalyst in mobile applications

Elisabetta M. CEPOLLARO[1], Stefano CIMINO[1], Michele E. Fortunato[1], Luciana LISI[*,1]
[1]*Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili (STEMS) – CNR, P.le Tecchio 80 – 80125 Napoli, Italy.*
** luciana.lisi@cnr.it*

Significance and Relevance

The development of H_2-fueled vehicles has been proposed to contribute to the limitation of the large fraction of CO_2 emissions associated to the transports sector because hydrogen is a carbon-free fuel. However, there are operating points of the engine promoting the formation of thermal NO_x. The use of H_2, already present on board as a fuel, for the Selective Catalytic Reduction (SCR) of NO_x, replacing ammonia, would avoid the additional device for storage and injection of urea.
ZSM5 supported Pt catalysts have been investigated for SCR of NO_x and the effect of additives considered to inhibit the undesired NO oxidation.

Preferred and 2nd choice for the topic: Automotive and stationary emission control
Preferred presentation: Poster

Introduction and Motivations

In order to mitigate the global warming limiting CO_2 emissions, the development of electric cars has been proposed as primary solution for the transports sector. Nevertheless, approaches still based on Internal Combustion Engine (ICE) have been also considered, such as the use of hydrogen as fuel. Since a completely NO_x free combustion cannot be ensured at all operating points[1] of the H_2-fueled engine which works under lean condition, a catalyzed exhaust after-treatment system is required. H_2 as a reducing agent of NO_x would have the advantage that only one fuel must be carried on board both for propulsion and NO_x reduction, thus avoiding the device for storage and injection of urea, as for the more common NH_3-SCR.
The NO_x reduction by H_2 produces only elemental nitrogen and water:

$$2\ NO + 4\ H_2 + O_2 \rightarrow N_2 + 4\ H_2O \qquad (1)$$

MFI zeolite supported Pt catalysts exhibited higher N_2 selectivity than metal oxide supported catalysts, however, in the presence of excess O_2, Pt can easily catalyse NO oxidation to NO_2[2,3]. In this work, the effect of Pt load at very low levels (0.1-1%) on the activity and selectivity and that of the addition of sodium to depress the oxidation activity of platinum have been investigated.

Materials and Methods

A commercial ZSM5 powder with a SiO_2/Al_2O_3 ratio=23 was impregnated with platinum using an aqueous solution of Tertraammineplatinum(II) chloride hydrate with a platinum/zeolite concentration ratio to obtain 0.1%Pt, 0.5 or 1wt% nominal load. Portions of 0.1%Pt/ZSM5 sample were impregnated with a sodium nitrate solution at different concentration to obtain 5 and 10% Na.
H_2-SCR experiments were carried out in a fixed bed reactor in the temperature range 50-450°C and were also simulated in a DRIFT environmental chamber to investigate the adsorbed NO_x species involved in the reaction.

Results and Discussion

Catalytic tests performed on Pt/Z catalysts with different platinum loads showed that the addition of an amount as low as 0.1%Pt promoted NO conversion to N_2 in the temperature range 80-200°C. The temperature corresponding to the maximum NO conversion decreased with Pt load. Nevertheless,

even with a so low Pt load, at T>200°C NO is mostly oxidized to NO_2. The addition of sodium strongly inhibited the undesired NO_2 formation and, unexpectedly, the N_2O production occurring simultaneously with the main SCR reaction (Fig.1). Catalysts were fully characterized (elemental analysis, XRD, porosimetric analysis, NH_3-TPD) to determine the role of Pt dispersion and of the acid properties on the catalytic performance.

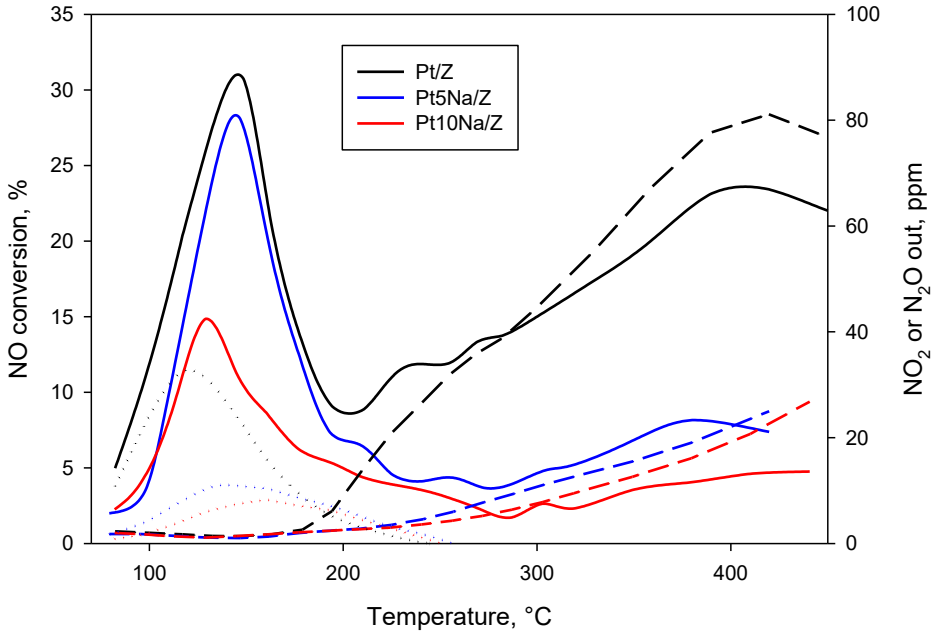


Fig. 1. NO conversion (solid line) and outlet concentration of NO_2 (dashed line) and N_2O (dotted line) of Pt/Z, Pt5Na/Z and Pt10Na/Z.

An Operando-DRIFT study was done to determine the role of adsorbed NOx species involved in the SCR reaction and to identify the possible reaction intermediates.

References

1. D. Koch, A. Sousa, D. Bertram, *SAE Technical Paper* **2019** 2019-01-2178.
2. Y. Guan, Y. Liu, Q. Lv, B. Wang D. Che, *J. Env. Chem. Eng*. 9 **2021** *9* 106770.
3. M. Machida, T. Watanabe, *Appl. Catal. B: Env.* **2004** *52* 281–286.

Acknowledgements

This research was funded by European Union – NextGeneration EU from the Italian Ministry of Environment and Energy Security POR H2 AdP MMES/ENEA with involvement of CNR and RSE, PNRR - Mission 2, Component 2, Investment 3.5 “Ricerca e sviluppo sull’idrogeno”, CUP: B93C22000630006

Effective upcycling of Pd(II) waste into an atomically precise Pd(II)-based catalyst for alkaline fuel cells applications

Francesco Montanari[*1], Marco Bonechi[1,2], Carlotta Cappanni[1], Pietro Gentilesca[1], Matteo Savastano[2,3], Mirko Severi[1], Antonio Bianchi[1,2], Massimo Innocenti[1,2]

[1]*University of Florence, Department of Chemistry "Ugo Schiff", Via della Lastruccia 3-13, 50019 Sesto Fiorentino, Italy.*

[2] *National Interuniversity Consortium of Material Science and Technology (INSTM), via G.Giusti 9, 50121, Italy.*

[3]*University San Raffaele Roma, Department of Human Sciences for the Promotion of Quality of Life, Via di Val Cannuta 247, 00166 Rome, Italy.*

** francesco.montanari@unifi.it*

Significance and Relevance

This work presents a novel approach toward the development of an efficient Pd(II)-based catalyst for the ORR in alkaline media. Selective extraction of Pd(II) from wastewater by functionalized multi-walled carbon nanotubes leads to excellent performance of the catalyst, reaching 90% H_2O production with comparable onset and half-wave potentials to bulk platinum electrodes while using only 1.94% of Pd(II). The assembly of the catalyst can be carried out under environmentally friendly conditions, at room temperature, in water and without a protected atmosphere. This approach couples waste management with sustainable energy production and furthers the circular economy approach for clean energy technologies.

Preferred and 2nd choice for the topic: Sustainable and clean energy production and transport and circular economy

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Complementing recent acts such as the European Green Deal, much emphasis has been directed toward the adaptation of renewable energy sources for clean energy production[1]. In this respect, resource-efficient waste management through upcycling metal waste into active electrocatalysts toward hydrogen-related reactions holds quite a central position in the concept of a circular economy[2]. The oxygen reduction reaction (ORR) is of prime importance to the efficiency of fuel cells, which may enable the use of chemical energy in electrical form with only water as a byproduct[3]. However, due to the intrinsically slow kinetics of the ORR, highly active electrocatalysts are still required for improving fuel cell performance. It is well known that the best catalysts, from an elemental composition point of view, are certainly the ones derived from platinum group metals (PGMs). Accordingly, with the limited availability and high cost of PGMs, efforts have been made to minimize their use in ORR electrocatalysts and recover them from wastewater as one of the important directions[4]. In this respect, atomically precise electrocatalysts are of peculiar interest due of their high atomic utilization efficiency, special electronic structure, and homogeneous distribution of active centers[5].

Results and Discussion

In the present study, we report the preparation of an atomically precise heterogeneous catalyst containing Pd(II) ions anchored on multi-walled carbon nanotubes and the results of its application in accelerating the ORR. The catalyst was prepared by selective and quantitative extraction of Pd(II) from the mixture of metal ions that usually accompany Pd(II) in wastewater from the processing of this metal. This approach enables the in situ transformation of Pd(II) waste into a valuable ORR catalyst. The process relies on the strategic selection of a ligand to functionalize the multi-walled carbon nanotubes MWCNT surface. The ligand consist in an unit which ensure stable coordination of the catalytic metal centre (Pd(II)) and in a unit capable of anchoring the complex on MNWCT. Notably, the entire assembly of the catalyst (MWCNT-LPd) is environmentally sustainable, proceeding spontaneously in water, at room temperature, without requiring a controlled atmosphere, and with minimal energy intake.

The successful extraction of Pd(II) was verified using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), confirming the highly selective and quantitative recovery of the metal. The

resulting catalyst (MWCNT-LPd) was thoroughly characterized using Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), and X-ray Photoelectron Spectroscopy (XPS), which confirmed the uniform distribution of Pd, the absence of competing metals, and the oxidation state of the coordinated Pd(II). Prior to electrochemical evaluations, the catalyst was treated with a Nafion polymeric dispersion to enhance its performance during rotating ring-disk electrode (RRDE) experiments. These studies explored the ORR catalytic mechanism and determined the number of electrons transferred per oxygen molecule. Electrochemical testing revealed a nearly complete 4-electron ORR pathway (90% H_2O production), with an onset potential of -0.118 V and a half-wave potential of -0.307 V. This performance is comparable to that of bulk platinum electrodes, demonstrating the catalyst's efficiency and cost-effectiveness as an alternative to platinum for fuel cells. Additionally, extended electrochemical testing confirmed the stability of MWCNT-LPd, showing no structural degradation or palladium loss.

The study successfully integrated waste management with sustainable energy production, transforming Pd(II)-containing waste into a robust and efficient ORR catalyst under environmentally benign conditions. This advance highlights a cost-effective alternative to platinum electrodes for fuel cells, placing emphasis on resource recovery and clean energy within a circular economy framework.

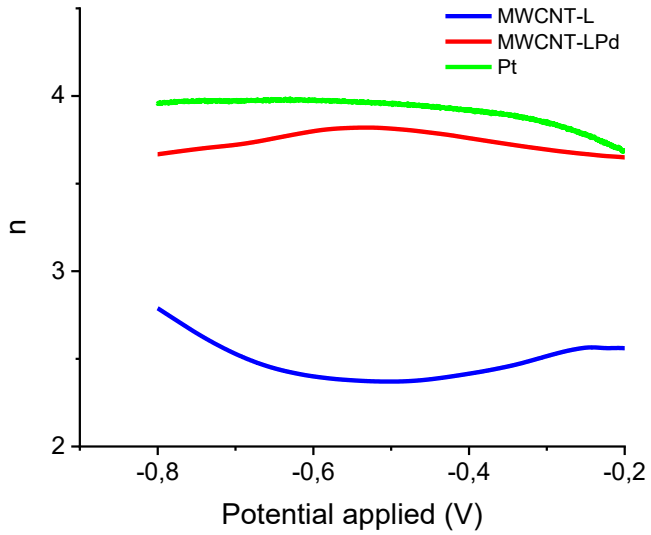


Figure 1: ORR electrocatalytic performance, KOH 0.1 M O_2 saturated solution, 1600 rpm rotation rate, 10 $mV \cdot s^{-1}$ scan rate. RRDE number of exchanged electrons per O_2 molecule (n) as function of the potential applied at the RRDE working electrode.

References

1. Montiel, M. A. *et al., Appl. Catal. B Environ.*, **2023**, *327, 122414.*
2. Chen, Z. *et al., Nano-Micro Lett.* **2022**, *15, 4.*
3. Bonechi, M. *et al., Catalysts,* **2021**, *11, 764.*
4. Monini, V. *et al., Dalton Trans.*, **2024**, *53, 2487-2500.*
5. Yan, L. *et al., Chem*, **2023**, 9, 280-342.

Acknowledgements

The authors acknowledge the support offered by Project 2022NW4P2T CUP B53D23013890006 "From metal nanoparticles to molecular complexes in electrocatalysis for green hydrogen evolution and simultaneous fine chemicals production" PRIN2022 Progetti di Ricerca di Rilevante Interesse Nazionale funded by Italian Ministry of University and Research and NextGenerationEU.

GAS-PHASE SELECTIVE DEHYDRODIMERIZATION OF 3-PICOLINE IN THE COHERENT SYNCHRONIZATION MODE

Nagieva I.T.[2], Malikova N.N.[1], Ali-zadeh N.I.[1], Nagiev T.M.[1]

[1]Nagiev Institute of Catalysis and Inorganic Chemistry of Ministry of Science and Education, Baku, Azerbaijan; [2]Baku State University, Baku, Azerbaijan

Currently, the economic need for nitrogen-containing heterocyclic compounds prompts the search for new effective technologies for their production. It should be added that pyridine and its derivatives are of particular interest, i.e. containing in addition to a carbon atom and a nitrogen atom. This gives these compounds a number of special properties. These properties include various types of fungicidal, pharmacological activity and others. Therefore, the synthesis of pyridine bases and their derivatives by fairly simple transformations, for example, dehydrogenation of the corresponding higher saturated compounds, is relevant. From this point of view, the synthesis of important pyridine bases using nitrous oxide without the use of catalysts is of theoretical and applied interest, since the reactions proceed using a simplified technology.

In recent decades, nitrous oxide has attracted increasing attention from researchers as a selective oxygen donor for the catalytic oxidation of hydrocarbons. It is particularly widely used in gas-phase oxidation of hydrocarbons.

This report presents the results of studies of coherently synchronized reactions of nitrous oxide decomposition and 3-picoline oxidation in the gas phase. Optimal conditions for obtaining target products in this reaction are revealed. The effect of process parameters on the yield of reaction products is shown. The regions of selective oxidation of 3-picoline are revealed and optimal conditions for obtaining target products are determined.

Experimental studies of the oxidation reaction of 3-picoline with nitrous oxide (1) were carried out in the temperature range of 580-610ºC. As a result of research, it was found that an increase in temperature from 580 to 610°C is accompanied by an increase in the yield of 3,3-ethylenedipyridine and 2,2-dipyridyl 3,3-dimethyl. This is due to the fact that, according to the equation, during the thermal decomposition of nitrogen oxide (1), the rate of formation of active centers (atomic oxygen) increases:

$$N_2O \longrightarrow N_2 + O^{\cdot}$$

Thus, dehydrodimerization of 3-picoline with the “green oxidizer” nitrogen oxide (1) in the gas phase at a temperature of 610°C leads mainly to the production of practically important products - 3,3-ethylenedipyridine and 2,2-dipyridyl-3,3-dimethyl, yield which respectively amounts to 26.8 wt.%. and 28.9 wt.%, with relatively high selectivity.

These studies show how, in the mode of coherent synchronization of the thermal decomposition of nitrogen oxide (1) and dehydrodimerization of 3-picoline, precursors necessary in the chemical, pharmaceutical, and petrochemical industries were obtained.

1. Nagieva I.T., Ali-zadeh N.I., Nagiev T.M. Coherent-Synchronized Oxidation of Pyridine with Nitrous Oxide to 2.2- and 2,3-Dipyridil../Journal of Chemistry and Chemical Engineering (USA), 2016. №10. p.99-102.

2. Nagieva I.T., Ali-zadeh N.I., Nagiev T.M. Coherent-Synchronized Reaction of Oxidation of Pyridine ”Green Oxidants” – H_2O_2 and N_2O. Scientific Reviews & Chemical Communications 2017, V.7, p1-8.

3.Nagieva I.T. Ali-zadeh N.I., Nagiev T.M. Gas-fase Oxidation of Piperidine with Nitrous Oxide to 2,3,4,5-tetrahidrohyridine. 23-rd International Congress of Chemical and Process Engneering CHISA 2018. 25-29 August. 2018.P1.43. p 451. Prague. Czech Republic.

Catalytic degradation of plastic wastes to valued materials

Shaobin WANG
[1]School of Chemical Engineering, The University of Adelaide, SA 5005, Australia.
* e-mail: Shaobin.wang@adelaide.edu.au

Significance and Relevance

Plastics are currently used widely in our daily life; however, poor management and disposal of plastic wastes result in their ubiquity throughout the biosphere. To date, there still lacks a comprehensive understanding of the sources, distribution, transport, and fate of microplastics (MPs) in different environmental compartments, which impedes the incisive establishment of efficient strategies toward addressing this problem. We recently review the wide issues of MP pollution and their control strategies and technologies and would present the recent work in conversion and degradation of MPs via catalytic processes.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion

Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster): Oral only

Introduction and Motivations

The soaring demands, production, and disposal of plastics have caused a great burden on the environment. Chemical degradation and catalytic transformation techniques are capable of decomposing or converting plastics into value-added chemicals, fuels, and functional nanocarbons. To this end, we have investigated the recent advances in carbon and hydrogen circulations by catalytic technologies in plastic chemistry and illustrated the overall fate and pathways of carbon and hydrogen elements from plastics (**Figure 1)**.[1]

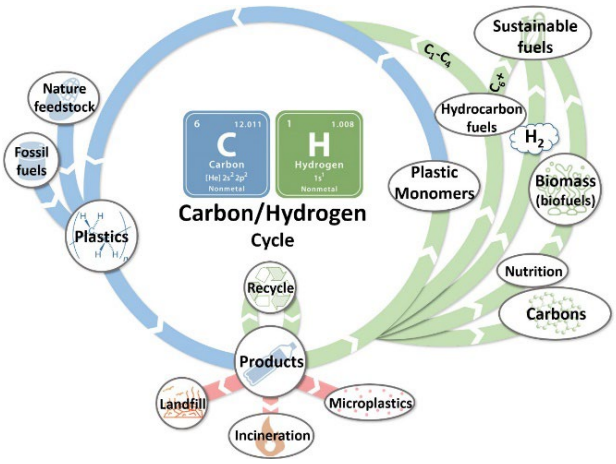


Figure 1 The flow of carbon and hydrogen in plastics. The blue, green and red routes represent the generation, recycling/upcycling, and dispose fate of plastics, respectively.

Results and Discussion

Advanced oxidation processes (AOPs) are emerging techniques for microplastics (MPs) purification. Firstly, a hydrothermal coupled Fenton system is developed for decomposition of ultrahigh molecular weight polyethylene, achieving 95.9% of weight loss in 16 h and 75.6% of mineralisation efficiency in 12 h. The system is also efficient to remediate different petroleum-based plastics and maintains high efficiency in practical water bodies (Figure 2).[2] Characterisations revealed a two-stage degradation process: chain unfolding/stretching and oxidation, giving rise to the formation of carbonyl groups and decreased crystallinity of MPs during the hydrothermal treatment. The chain stretching stage is pivotal

to the whole treatment because it remarkably facilitates subsequent chain cleavage and Fenton oxidation.

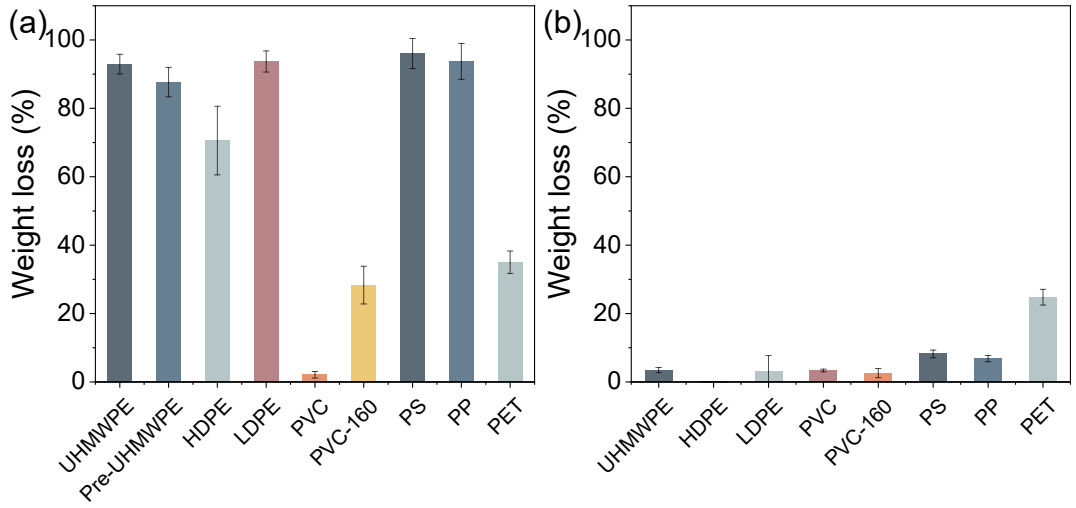


Figure 2. Weight loss of different types of microplastics (a) after thermal assisted Fenton treatment, and (b) thermal treatment with 0.2 M H^+ (experimental conditions: Fe^{2+}: 4 mM, H_2O_2: 200 mM, MPs: 1 g L^{-1}, temperature: 140 °C).

In addition, we demonstrated a bimetal-carbon-activated peroxymonosulfate (PMS) Fenton-like system for effectively converting polypropylene into hydrocarbons and ketones.[3] In a hydrothermal reaction process at 160 °C for 14 h, directional polypropylene conversion was achieved at a selectivity of 80 wt% hydrocarbons and ketones in the products. The efficient breaking of C-C/C-H bond in polypropylene and the subsequent further oxidation under mild conditions led to the dominated products of hydrocarbons and ketones.

Overall, in aqueous environment, MPs can cause potential physical injuries to microorganisms and act as carriers of detrimental pollutants. Heterogeneous Fenton-like system can not only alleviate the increasingly serious white pollution problem as it has the virtue of high efficiency, low toxicity, and effectiveness in aqueous environment, but also realize the circular economy of plastics. It is of great significance for the establishment of a sustainable society. Future research opportunities can be the development of Fenton-like systems for MPs remediation with greater applicability with a boarder pH working window, lower reaction temperature, and reduced oxidant usage.

References

1. Kunsheng Hu, Yangyang Yang, Yuxian Wang, Xiaoguang Duan, Shaobin Wang, Catalytic carbon and hydrogen cycles in plastics chemistry, *Chem Catal*., 2022, 2, 724-761.
2. Kunsheng Hu, Peng Zhou, Yangyang Yang, Tony Hall, Gang Nie, Yu Yao, Xiaoguang Duan, Shaobin Wang, Microplastics degradation by thermal Fenton reaction, *ACS ES&T Eng.*, 2022, 2, 110–120.
3. Jingya Ye, Ning Li, Wenjie Gao, Wenchao Peng, Xiaoming Peng, Zhanjun Cheng, Beibei Yan, Yao Fu, Sihui Zhan, Guanyi Chen, Shaobin Wang, Bimetal-carbon engineering for polypropylene conversion into hydrocarbons and ketones in a Fenton-like system, *Appl. Catal. B: Environ.* & *Energy*, 2024, 358, 124411.

On the structure reactivity and synthesis strategy of mixed-oxides prepared by microwave-assisted solution combustion synthesis – XAS and XRD operando study

Paulina SUMMA[1,2], Katarzyna ŚWIRK DA COSTA [3], Li LI [4], Magnus RØNNING [3], Monika MOTAK [2], Marta GAJEWSKA [5], Changwei HU [4], Patrick DA COSTA [1,*]

[1] *Sorbonne Université, Institut Jean Le Rond d'Alembert, CNRS UMR 7190, 2 pl. de la gare de ceinture, Saint-Cyr-L'Ecole, France*

[2] *AGH University of Science and Technology, Faculty of Energy and Fuels, Al. A. Mickiewicza 30, Kraków, Poland*

[3] *Norwegian University of Science and Technology, Department of Chemical Engineering, Sem Sælands vei 4, Trondheim, Norway*

[4] *Sichuan University, Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Chengdu, PR China*

[5] *AGH University of Science and Technology, Academic Centre for Materials and Nanotechnology, Al. A. Mickiewicza 30, Kraków, Poland*

** patrick.da_costa@upmc.fr*

Significance and Relevance

One of the most optimal regarding the economic perspective and catalytic performance, compositions of CO_2 methanation catalyst consists of Ni as an active phase and mixed Al_2O_3-MgO support. Typically, to obtain strong metal-support interaction and form well-dispersed surface nickel nano-crystallites, such catalyst was produced via thermal decomposition of hydrotalcites.[1] To optimize the synthesis protocol, and eliminate energy consuming steps such as precipitation, drying and calcination, thermal solution combustion synthesis (T-SCS) has been successfully applied. It was reported that T-SCS derived catalysts resulted in enhanced catalytic performance compared to the hydrotalcite-derived counterpart.[2] Another improvement, to limit the time and energy delivered to the synthesis was application of microwave reactor as a heat source (M-SCS). With this approach, it was possible to obtain the Ni-Mg-Al catalyst with excellent properties in a preparation protocol shorter than 10 minutes.

Preferred and 2nd choice for the topic: Oral preferred or Short Oral

Introduction and Motivations

CO_2 hydrogenation to methane brings a promising perspective for conversion of carbon dioxide into the desired synthetic natural gas (SNG), due to the simplicity of the process (ambient pressure of the reaction, relatively low temperature range 250-450 °C) allowing simplified scalability, finding its confirmation in the increasing number of plants introduced worldwide. Nickel catalyst is the best compromise between the good catalytic performance and costs of production. Presence of alumina in the support enhances specific surface area, and inhibits Ni sintering, MgO delivers surface basicity necessary for adsorption and activation of carbon dioxide.[1,2]

Materials and Methods

Initially, solution containing nitrate precursors $Ni(NO_3)_2{\cdot}6H_2O$ (Chempur, p.a.), $Mg(NO_3)_2{\cdot}6H_2O$ (Sigma Aldrich, p.a.), $Al(NO_3)_3{\cdot}9H_2O$ (Chempur, p.a.) with desired amount of urea (100 or 175%) was complexed for 40 minutes on the magnetic stirrer, at 50 °C. Later, solution in the Pyrex beaker was placed inside the microwave reactor set for 800 or 1000 W, and heated till the combustion was completed.

Table 1. List of the studied samples in regard to the synthesis conditions

Catalyst	Urea content [%]	Microwave power [W]
SCS_100_800	100	800
SCS_175_800	175	800
SCS_100_1000	100	1000
SCS_175_1000	175	1000

CO_2 methanation reaction tests were performed with the use of a tubular fixed-bed quartz U-type reactor under the following conditions: $CO_2/H_2/Ar$ of 1.5/6/2.5, with a total flow of 100 ml/min, GHSV of 12 000 h^{-1}, 1 bar, t from 250 to 450 °C.

The catalysts were characterized using the following methods: ICP-MS, low-temperature N_2 sorption, H_2-TPR, CO_2-TPD, TEM, XPS. In-situ XRD, XAS and EXAFS were performed at the Swiss-Norwegian beamline (SNBL, BM31) at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France).

Results and Discussion

Results of temperature-programmed surface reaction measured at steady-state (TPSR) are compared in Fig. 1. It is visible that both catalysts synthesized with the above-stoichiometric urea content resulted in superior catalytic performance. CO_2 conversion of SCS_175_800 and SCS_175_1000 is almost identical, which suggests that in this case, the increase of the microwave power output did not bring any beneficial effect. On the other hand, for the catalysts prepared with stoichiometric urea amount (SCS_100_800, SCS_100_1000), the observed catalytic conversions are lower, than in the case of counterparts obtained at above-stoichiometric urea contribution. The CO_2 conversion is visibly improved, in the SCS_100_1000 sample at 300 °C, compared to the SCS_100_800, suggesting that the certain dynamics of the combustion (provided either from the heat energy delivered to the system (1000 W) or fuel decomposition) is essential to form a reactive interface with an enhanced activity. The synthesis conditions, in particular the urea/(Ni+Mg) ratio has an impact on the physico-chemical properties. The use of stoichiometric urea amount resulted in better development of surface basicity confirmed with CO_2-TPD.

On the contrary, the above stoichiometric fuel content resulted in an improvement development of nano pores at the surface, while higher used power (1000 W) contributed to increase in S_{BET} of ca 30%. Furthermore, with an increase of energy delivered to the synthesis (fuel+power) the shift towards higher 2θ in XRD reflection corresponding to MgO (200) at 42.9 deg was registered, suggesting a deficit of oxygen in the lattice. During the operando XAS-XRD measurement, it was observed that among all the studied samples, SCS_175_800 is remaining the least reduced after the reaction. It suggests that surface reactivity of this catalyst is more effective than for other materials – incomplete reduction of nickel preserved the oxygen at the surface, allowing formation of additional basic sites and activation of CO_2.

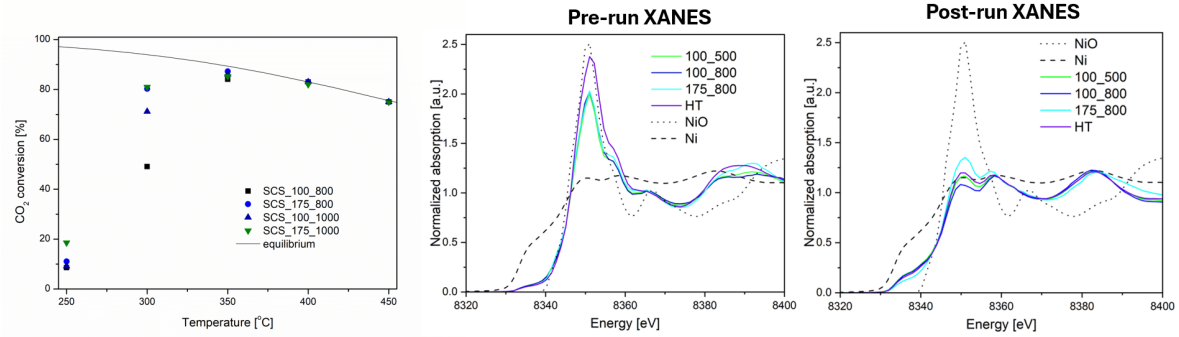


Figure 1. CO_2 conversion of the M-SCS catalysts (left), XANES spectra comparing the M-SCS (100_800, 175_800) samples with hydrotalcite-derived (HT) and T-SCS (100_500), before the in-situ catalytic reaction (middle), after in-situ catalytic reaction (right).

References

1. D. Wierzbicki, R. Baran, R. Dębek, T. Grzybek, et al., Int. J. Hyd. Energy, **2017**, 42, 37, 23548
2. P. Summa, M. Gajewska, L. Li, C. Hu, et al., J. CO_2 Util., **2022**, 60, 101983

Acknowledgements

Paulina Summa acknowledges the French Embassy in Poland for providing the BGF Doctorate Cotutelle scholarship. Katarzyna Świrk Da Costa is MSCA-IF researcher at the Norwegian University of Science and Technology in Norway. This project has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No 892571. The project team at SNBL is acknowledged for experimental assistance (SNBL-BM31).

Comparative assessment of power-to-methane technologies for sustainable synthetic natural gas production

Oscar FURST[1], Daniel SCHMIDER[2], Julian DAILLY[2], Olaf DEUTSCHMANN[*,1]
[1]*Karlsruhe Institute of Technology, Institute for Chemical Technology and Polymer Chemistry, Kaiserstraße 12, Karlsruhe, Germany.*
[2]*European Institute for Energy Research, Emmy-Noether-Straße 11, Karlsruhe, Germany.*
** deutschmann@kit.edu*

Significance and Relevance

In this study, 20 Power-to-Methane (PtM) plant concepts which integrate Solid Oxide Electrolysis Cells (SOECs) and various carbon capture technologies are optimized. The high efficiencies of the PtM systems achieved in this study highlight the significant efficiency gains from thermal integration of carbon capture processes by up to 8.4%. Additionally, the study demonstrated that exothermic SOEC operation can reduce capital expenditures with minimal plant efficiency loss, providing a new perspective on optimizing PtM systems for renewable fuel production.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling, catalysis to electrify the chemical production
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The Power-to-Methane (PtM) technology offers a promising pathway to decarbonize the automotive industry by converting renewable electricity into methane, a sustainable fuel alternative when it is produced from captured CO_2[1]. When it integrates the carbon capture process, the technology not only provides a means to store excess renewable energy but also negates the overall greenhouse gas emissions of the downstream processes. The efficiency and viability of the technology can be enhanced by utilizing SOECs, supporting the transition to cleaner transportation solutions[2].

Materials and Methods

20 different PtM plant concepts are created by combining different methanation, SOEC and carbon capture technologies. Fixed-bed methanation reactors and three-phase methanation reactors are considered as methanation technologies, while electrolyte-supported and cathode-supported SOEC are studied as possible electrolysis technologies. The PtM plant concepts include a CO/CO_2 supply from either biomass gasification, amine gas treatment or direct air capture. A flexible simulation tool developed in Matlab simulates the plant concepts under different operating conditions, which are simultaneously optimized for maximum efficiency while considering constraints like temperature gradients in the electrolyzer and suitable Synthetic Natural Gas (SNG) output.

Results and Discussion

The optimization of the PtM process chains shows that the selected processes with integrated carbon capture technologies can reach high power to methane efficiencies of up to 84.6% with ideal thermal integration. Even when CO_2 is separated through the energy intensive direct air capture technology, plant high heating value efficiency can reach up to 74.8%. Specifically, it is the thermal integration of the carbon capture process with the methanation and electrolysis processes which allows to raise the efficiency of the combined plant by 8.4% compared to separated direct air capture and PtM facilities. The magnitude of this increase in efficiency makes the use of direct air capture a more realistic perspective.

Through a sensitivity analysis, the gas temperature at the inlet of the electrolyzer was identified as the operating parameter with the highest impact on the total plant efficiency by a large margin, owing to the increased electrical efficiency of SOEC at high temperatures and the possibility of using resistive

heating to circumvent the losses incurred by the power rectifiers needed to operate SOEC with direct current.

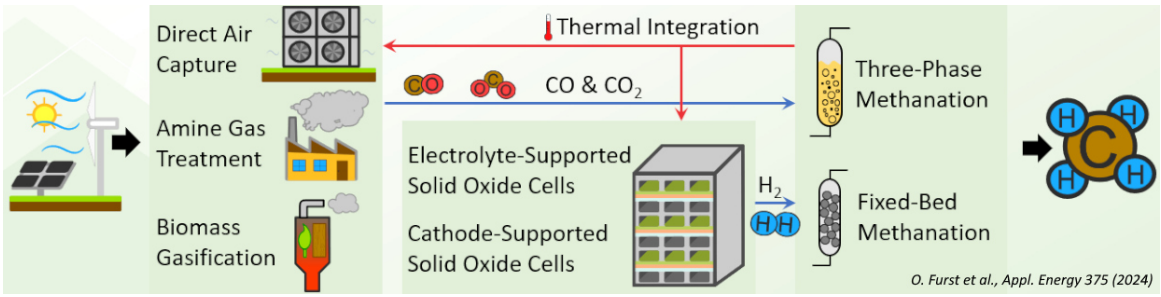


Figure 1: Visualization of the possible permutations of technologies selected to assemble 20 thermally integrated PtM plant concepts[3].

In addition, sweep gas recirculation in the SOEC was shown to lead to a substantial increase in PtM efficiency of up to 6.8% by reducing the amount of sweep gas heating required and by allowing the electrolyzers to be operated under pressure without the need to compress the sweep gas.

Finally, drawing the pareto front of a bi-objective optimization of the plant efficiency and number of electrolysis stacks required in the plant reveals that exothermic operation of the electrolyzers can allow to substantially reduce the amount of electrolyzers required without significantly impacting the plant efficiency, potentially allowing a large reduction of investment costs.

Through the comparison of a large number of PtM process chains, this study provides valuable insights into process optimizations which may greatly bolster the viability of sustainable SNG production.

References

1. M. Sterner, I. Stadler, *Energiespeicher – Bedarf, Technologien, Integration*, Springer Berlin Heidelberg **2014**.
2. D. Parra, X. Zhang, C. Bauer, M. Patel, *Applied Energy* **2017**, *193*, 440-454.
3. O. Furst, L. Wehrle, D. Schmider, J. Dailly, O. Deutschmann, *Applied Energy* **2024**, *375*, 123972.

Acknowledgements

This work was supported by the German federal ministry for economic affairs and energy (Bundesministerium für Wirtschaft und Energie, BMWi) [grant numbers 03EIV041D, 03EIV041E] in the "MethFuel" group of the collaborative research project "MethQuest". The authors acknowledge support by the state of Baden-Württemberg through bwHPC.

Omegadot software and consulting GmbH is gratefully acknowledged for a cost-free academic license of DETCHEM.

Parts of the results of this study have been published in Applied Energy[3].

Water Inhibition of NH_3-SCR over Cu-CHA: Measurements and DFT-based kinetic modeling

Shivangi Singh,[a,b] Yingxin Feng[a], Ton V. W. Janssens[b], and Henrik Grönbeck[a]
[a]Department of Physics and Competence Centre for Catalysis, Chalmers University of Technology, SE-412 96 Göteborg, Sweden
[b]Umicore Denmark ApS, DK-2970 Hørsholm, Denmark

Significance and Relevance

Understanding the interaction between water and zeolite catalysts is vital not only for diesel exhaust treatment but also extends to exhaust systems for hydrogen combustion in internal combustion engines (ICEs), where water vapor is present in large amounts. Water is measured to significantly impact ammonia-selective catalytic reduction (NH_3-SCR) over Cu-CHA. Atomic-level understanding is provided by a DFT-based kinetic model.

Preferred and 2nd choice for the topic:
Automotive and stationary emissions control
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Cu-exchanged chabazite (Cu-CHA) is a widely applied catalyst for selective catalytic reduction of nitrogen oxides in oxygen excess.[1] However, the potential application of Cu-CHA in hydrogen-fueled internal combustion engines (H_2-ICEs) presents new challenges due to the high partial pressures of water vapor produced during hydrogen combustion.[2]

Herein, we present flow reactor measurements to study the NH_3-SCR rate over Cu-CHA with H_2O partial pressures in the range from 2% to 25%. The measurements are corroborated with Density Functional Theory (DFT) calculations and DFT-based microkinetic modeling to understand the atomic-level mechanisms for the H_2O inhibition of the NH_3-SCR reaction.

Materials and Methods

A Cu-CHA catalyst (Si/Al = 6.7, 3.2 wt% Cu) was prepared via Cu-nitrate impregnation and calcination (600 °C, 2 h). For SCR measurements, 4 mg catalyst (150–300 µm) mixed with 76 mg SiC was degreened (10% O_2, 500 °C, 30 min) and exposed to 500 ppm NO, 600 ppm NH_3, 10% O_2, and 2–25% H_2O in N_2 at 200 °C, at the flow rate of 18 NL/h.
Density functional theory (DFT) calculations were performed using the Vienna Ab- Initio Simulation Package (VASP). Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional with Hubbard- U and van der Waals corrections was applied using a plane wave basis with the kinetic energy cutoff at 480 eV. The chabazite structure is described with a periodic rhombohedral unit cell, which contains 12 tetrahedral Si-sites. We use the experimentally determined lattice parameters which are fixed during the structural optimizations.

Results and Discussion

The effect of water on the NO_x conversion is studied under dry and wet conditions (5% water). We find that water reduced the conversion in the temperature range of 160°C to 260°C. Measuring the NO_x conversion for pressures in the range from 0% to 25% at 200°C supports this trend, with a reduction in NO_x conversion for water pressures higher than 2%. The NO_x conversion is used to calculate the reaction order with respect to water, we find a change in the reaction order in water from -0.16 at 2% water to -1.11 at 25% water. The measured reaction order for water follows the simple equation: $-3.23 \cdot \exp(0.76 \cdot \ln(p(H_2O)))$ as shown figure 1 (A).

Density functional theory (DFT) calculations are performed to explore the mechanism for water inhibition. The calculations investigate water adsorption on key intermediates in a previously

suggested reaction cycle [3,4]. O_2 is at low temperatures activated by adsorption on a pair of NH_3-solvated Cu+ species $[Cu^+(NH_3)_2]$ forming a Cu-peroxo species, $[Cu_2(NH_3)_4O_2]_2^+$. NH_3 and NO couple twice over the Cu-peroxo species, resulting in the formation of two H_2NNO and a $[Cu_2(NH_3)_4OHOH]^{2+}$ complex. Previous simulations indicate that $[Cu_2(NH_3)_4O_2]_2^+$ and $[Cu_2(NH_3)_4OHOH]^{2+}$ together with $[Cu_2(NH_3)_5O_2]_2^+$ are the most abundant intermediates at temperatures around 200°C [3,4]. The present DFT calculations show that H_2O adsorption competes with NO adsorption on the Cu-sites on $[Cu_2(NH_3)_4O_2]_2^+$ and $[Cu_2(NH_3)_4OHOH]^{2+}$.

By accounting for H_2O adsorption in the DFT-based microkinetic model [4], we are able to reproduce the experimentally measured reaction orders, which supports the inhibitory effect of H_2O. The simulated TOF aligns well with experimental data when slight adjustments have been done to the H_2O entropy of adsorption as well as a weak partial pressure-dependent term in the H_2O Gibbs free energy of adsorption is introduced as shown in Figure 1(B).

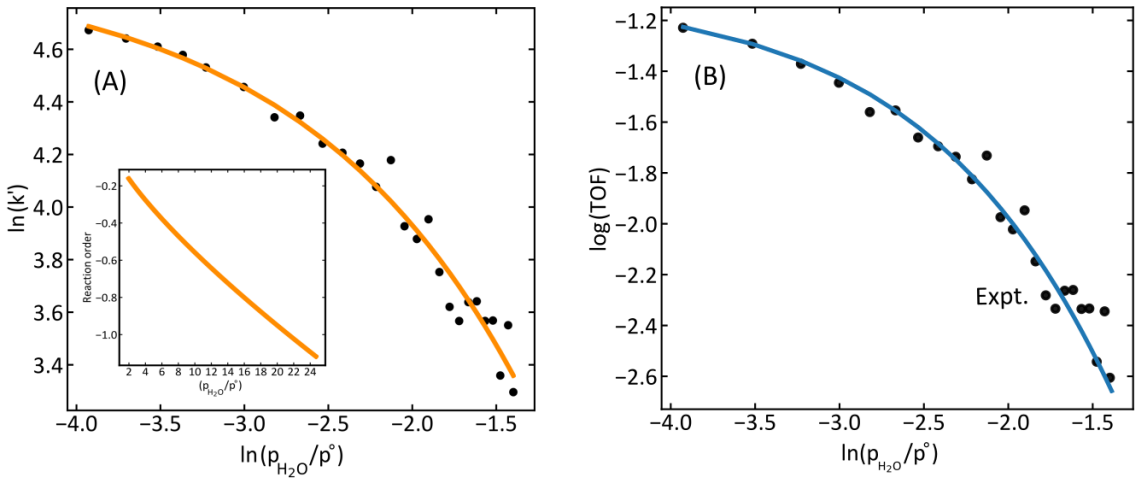


Figure 1: (A) Natural logarithm of the rate constant ln(k') as a function of the natural logarithm of partial pressures of water and (B) Logarithm of simulated TOF as a function of logarithm of the partial pressures of water.

References

[1] A.M. Beale et al., *Chem. Soc. Rev.*, **2015**, *44*, 7371-7405.
[2] C.M. White et al., *Int. J. Hydrogen Energy*, **2006**, *31*, 1292-1305.
[3] L. Chen et al., *ACS Catal.*, **2020**, *10*, 5646-5656.
[4] Y. Feng et al., *ACS Catal.*, **2021**, *11*, 14395-14407.

Acknowledgements

We acknowledge support from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement no. 955839 (CHASS). The calculations have been performed at PDC (Stockholm) and NSC (Linköping) through a NAISS grant (2022/3-14). The Competence Centre for Catalysis (KCK) is hosted by Chalmers University of Technology and financially supported by the Swedish Energy Agency (52689-1) and the member companies Johnson Matthey, Perstorp, Powercell, Preem, Scania CV, Umicore and Volvo Group.

Enhancing Low-Temperature CO_2 Methanation: The Role of Praseodymium Oxide in Ni-Based Catalysts

Yanggeun[1], Junseo Park[1], Sung Bong Kang[*,1]
[1]*School of Environment and Energy Engineering, Gwangju Institute of Science and Technology, Gwangju, 61005, Republic of Korea*
** sbkang@gist.ac.kr*

Significance and Relevance

The Ni/PrO_x (Nickel/Praseodymium oxide) catalyst developed in this study effectively achieve crucial challenge of thermodynamic limitation in CO_2 methanation by enhancing CH_4 selectivity and CO_2 conversion rates at low temperature ranges (250 to 350 °C). Through the unique oxygen mobility and formation oxygen vacancies property of PrO_x, CO_2 activation pathway are significantly improved. This approach overcomes the high kinetic barrier for low temperature CO_2 activation. Our findings demonstrate the potential of PrO_x utilization for development enhanced low temperature performance catalyst by experimental validation.

Preferred and 2nd choice for the topic: 1st CO_2 utilization and recycling, 2nd H_2 storage and transportation, green H_2 production, hydrogen vectors
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Research on nickel-based CO_2 methanation catalyst has been actively studied due to their relative advantage of cost-effectiveness rather than noble metals. However, the nickel catalysts require high temperature (above 300 °C) for achieving significant CO_2 methanation activity. [1] This limitation is due to the high kinetic barrier of CO_2 activation step, which require suitable catalyst surface properties for enhancing CO_2 activation.[2] Based on the theoretical background, we aimed to enhance low temperature activity by PrO_x based nickel catalyst which could provide electron donor sties suitable for improved CO_2 activation.

Results and Discussion

In Fig. 1 activity test comparing with conventional support based catalysts, Ni/PrO_x shows exceptional low temperature activity. The trend in T_{50} (the temperature at which 50% of CO_2 is converted) was observed as follows: Ni/PrO_x (253 °C) < Ni/Al_2O_3 (322 °C) < Ni/SiO_2 (379 °C). Also, the highest CH_4 selectivity on entire temperature range was observed. This result indicates that PrO_x support enhance low temperature activity and CO_2 hydrogenation pathway compared to other conventional supports in same nickel loading condition. The exceptional activity of Ni/PrO_x is closely associated with Its superior CO_2 activation ability in low temperature range, as observerd in Fig. 1 (c). The peak observed on 211 °C indicates that Ni/PrO_x surface was appropriate for the direct CO_2 decomposition to CO at low temperatures ($CO_2 \rightarrow CO + O^*$). The direct CO route for CO_2 methanation on Ni/PrO_x support present appropriate reaction pathway of CO_2 hydrogenation to CH_4.This enhancement of CO_2 activation behavior is clearly associated to surface chemical property, specifically electron donor properties.

To elucidate the correlation between improvement of CO_2 activation and PrO_x support properties, we focused on structural oxygen mobility and vacancies formation behavior of PrO_x. The structural oxygen mobility induces evacuation of structural oxygen and provide abundant oxygen vacancies for electron donor for activating CO_2 to CO and O*. Fig. 2 presents our analytic characterizations for elucidating PrO_x oxygen mobility property. In Fig. 2 (a), the structural oxygen evacuation profile result suggests high oxygen mobility of Ni/PrO_x and evacuation behavior in reduction condition. The oxygen mobility, as a property that induce superior oxygen vacancies formation, was investigated through Raman spectroscopy and Pr 3d XPS results. Through quantitative analysis of results in Fig. 2 (b), I_D/I_{F2g}

ratio (intensity ratio of the Defects band to the F_{2g} band), from 0.28 to 0.33 respectively, was observed. This result indicates that PrO_x was transformed oxygen deficiency oxide phase which has abundant electron donor sites. In Fig. 2 (c), Pr 3d XPS clearly supported the electron properties of Ni/PrO_x. The $Pr3^+/Pr^{4+}$ ratio of Ni/PrO_x increase from 0.85 to 0.96 respectively according to H_2 treatment. This results indicates that Ni/PrO_x surface has superior oxygen vacancies formation and high electron donating properties induced by oxide phase transformation.

Through characterization and activity test, we clearly observed exceptional low temperature activity and abundant oxygen vacancies formation induced by PrO_x support effects on surface of catalyst. This combined results suggests that the PrO_x provides suitable chemical properties to reduce the kinetic barrier of CO_2 activation at low temperature by formation oxygen vacancies which serve as electron donor sites for CO_2 adsorption and activation. This advantage in the reaction mechanism directly influenced on enhancement of low temperature catalytic activity of Ni/PrO_x. In conclusion, our study demonstrates the potential of PrO_x in enhancing low-temperature CO_2 methanation by comprehensive experimental analysis.

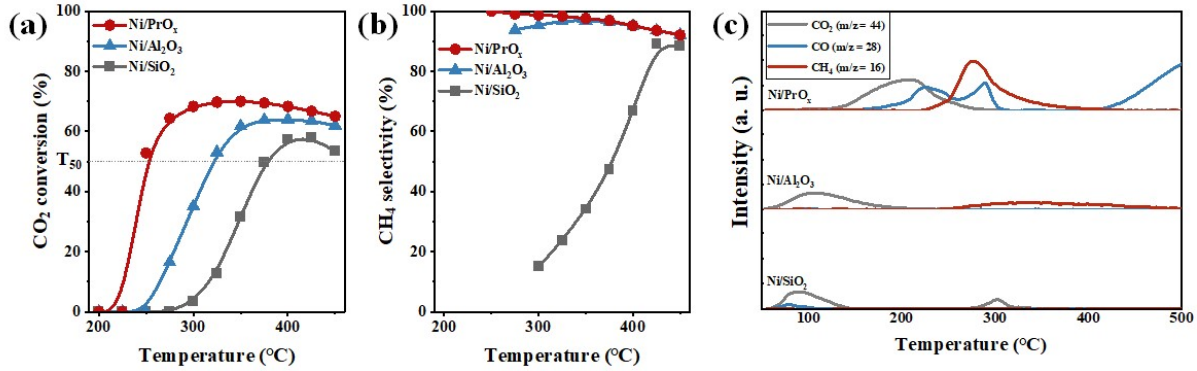


Fig. 1. (a) CO_2 conversion, (b) CH_4 selectivity and (c) CO_2-TPSR profile of Ni/PrO_x, Ni/Al_2O_3 and Ni/SiO_2 catalysts.

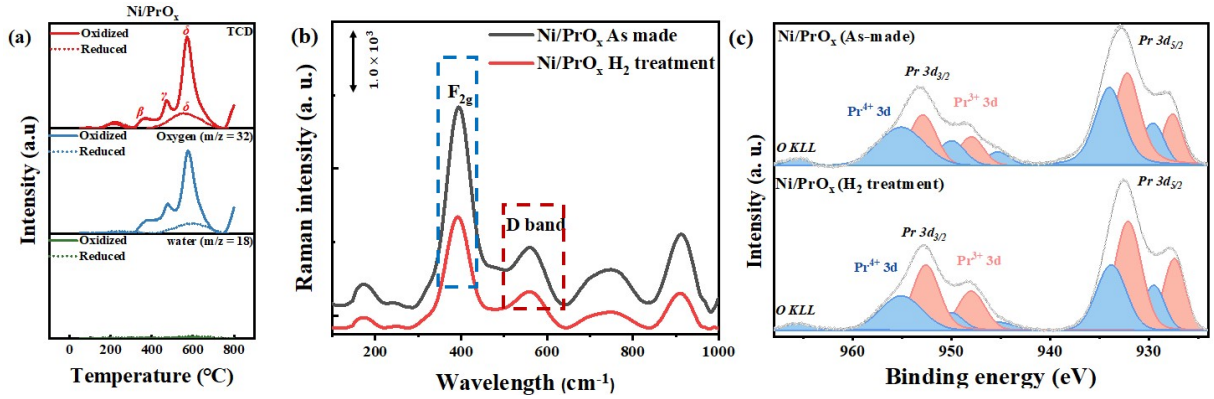


Fig. 2. (a) Structural oxygen evacuation, (b) Raman spectroscopy and (c) Pr 3d XPS profiles of Ni/PrO_x catalyst.

References

1. L. Shen, J. Xu, M. Zhu, Y.-F. Han, *ACS Catal*. **2020,** *10(24),* 14581-14591.
2. T. Zhang, W. Wang, F. Gu, W. Xu, J. Zhang, Z. Li, T. Zhu, G. Xu, Z. Zhong, F. Su, *Appl. Catal. B: Environ.* **2022,** *312*, 121385-121400.

Acknowledgements

This study was supported by the National Research Foundation of Korea (NRF) Grant funded by the Korean government (MSIT) (No. 2021R1C1C1005404, 2021R1A5A1028138).

Zirconia-based inorganic oxide catalysts for the abatement of highly toxic agrochemicals and chemical warfare agent simulants

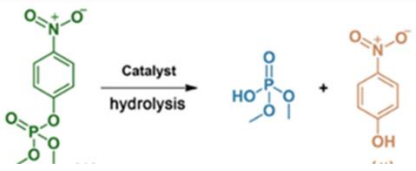
Stefano ECONDI[1], Nicola SCOTTI[1], Filippo BOSSOLA[1], Stefano MARCHESI[2], Chiara BISIO[1,2], Fabio CARNIATO[2], Matteo GUIDOTTI[*1]
[1]*CNR-SCITEC, via Golgi 19, Milan, Italy*
[2]*DISIT, University of Eastern Piedmont "Amedeo Avogadro", via Michel 11, Alessandria, Italy*
**matteo.guidotti@scitec.cnr.it*

Zr-containing inorganic oxides and metal-organic frameworks are attracting an ever-growing interest as heterogeneous catalysts for the degradation and abatement of highly hazardous organophosphorus compounds, that are toxic ingredients of polluting obsolete agrochemicals (*e.g.*, paraoxon, parathion, malathion) and anticholinergic nerve chemical warfare agents (*e.g.*, sarin, soman).[1]

The ability of Zr-O-Zr surface domains to effectively degrade organophosphorus esters is widely attributed to a hydrolytic capability similar to the Zn(II) multinuclear metal sites in phosphatase enzymes.[2] Thanks to a fine tuning of the arrangement and distribution of Zr centers at the inorganic oxide surface, it is possible to optimize the rapid and safe degradation and decontamination of hazardous organophosphates.

The present study aims at investigating how the density of exposed and accessible Zr(IV) species at the surface of a mesoporous zirconia-silica mixed oxide solid affects the capability to degrade the pesticide paraoxon (diethyl 4-nitrophenyl phosphate, obsolete agrochemical and nerve agent simulant) into non-noxious products, under very mild conditions, at ambient temperature and pressure. A set of ZrO_2-SiO_2 non-ordered mesoporous mixed oxide materials was prepared with a variable percentage of zirconia, namely, 100, 90, 70 and 50 (wt.%). Pure ZrO_2 (100%) was used in two forms: a tailor-made mesoporous high specific surface area and a reference low surface area bulk oxide obtained from commerce (Merck). The solids were fully characterized in terms of porosimetric, morphologic and physico-chemical properties. In particular, the acid and basic sites on the surface were thoroughly evaluated and quantified by means of in-situ FT-IR characterization by probe molecules.[3]

The catalysts (40 mg) were tested in the hydrolytic degradation of paraoxon (220 ppm solution) in liquid-phase batch reactor, in ethyl acetate as a solvent, at 20°C and 1 bar. Phosphoric acid derivatives and p-nitrophenol were the main observed products (Fig. 1).



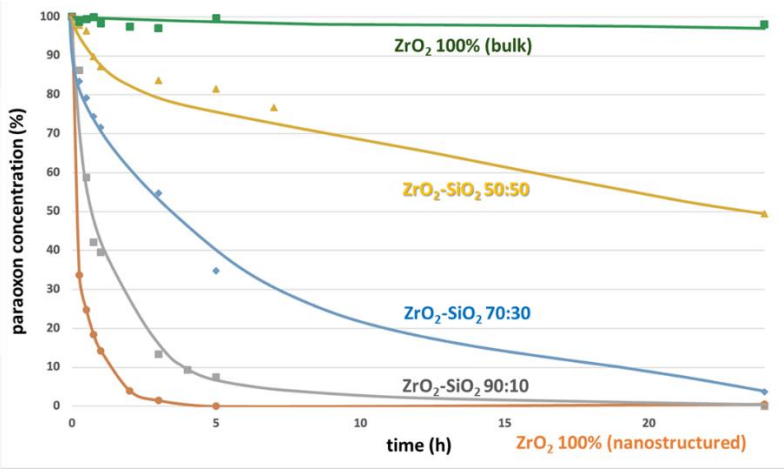


Fig. 1. Hydrolytic degradation of paraoxon over Zr-Si mixed oxides Reaction conditions: 220 ppm paraoxon; 40 mg catalyst; anhydrous AcOEt; 293 K; 1 bar

Nanostructured catalysts with high contents in ZrO_2 showed optimal performance and paraoxon was completely and selectively degraded into non-noxious derivatives with half-life times in the order of 15-30 min. Commercial bulk ZrO_2 showed virtually no activity under the same conditions. The most

active ZrO_2 catalyst was successfully recovered and reused in a new catalytic cycle up to 3 times, with a full recovery of its performance after a mild rinsing in polar solvents.

A clear correlation between the conversion of the pollutant and the amount of surface acid + basic sites on the catalysts was observed. The results evidenced a remarkable joint action of acid and, especially, basic sites in organophosphate hydrolysis. This study paves the path to a better understanding of the role of surface Zr-O-Zr-like aggregates at the surface of zirconia-containing oxides and the synergistic effect of both acid and basic sites in the catalytic safe and sustainable degradation of organophosphorus pollutants and contaminants.

References

1. S. Econdi, A. Caselli, S. Marchesi, F. Carniato, C. Bisio, M. Guidotti, *Eur. Phys. J. Plus*, **2024**, *139*, 782.
2. M. J. Katz, J. E. Mondloch, R. K. Totten, J. K. Park, S. T. Nguyen, O. K. Farha, J. T. Hupp, *Angew. Chem. Int. Ed.*, **2014**, *53(2)*, 497.
3. F. Zaccheria, F. Bossola, N. Scotti, C. Evangelisti, V. Dal Santo, N. Ravasio, *Catal. Sci. Technol.*, **2020**, *10*, 7502.

Acknowledgements

This work was supported by Progetti@CNR 2020 program (project “PerBiocid”, grant no. SAC.AD002.173.032).

Low Temperature-Water Gas Shift Reaction Using Perovskite-type Oxide Catalyst Containing Cerium Ion

Hidenori YAHIRO[1*], Noa YAMAGUCHI[1], Satoshi TOSHIOKA[1], Hiroyuki YAMAURA[1], Syuhei YAMAGUCHI[1], Anna Paola PANUNZI[2], Leonardo DURANTI[2], Elisabetta Di BARTOLOMEO[2]

[1]*Graduate School of Science and Engineering, Ehime University, Matsuyama 790-8577, Japan*

[2]*Department of Chemical Sciences and Technologies, University of Rome Tor Vergata, via della Ricerca Scientifica, 00133 Rome, Italy*

** hyahiro@ehime-u.ac.jp*

Significance and Relevance

The perovskite-type oxides containing Ce ion were successfully prepared by the thermal decomposition of heteronuclear metal cyano complexes. The present of trivalent Ce ion at A-site of perovskite-type oxide (ABO_3) was confirmed by several techniques. $Ni/La_{0.7}Ce_{0.3}FeO_3$ catalyst showed higher catalytic activity for the reverse water gas shift reaction ($CO_2 + H_2 \rightleftarrows CO + H_2O$) at low temperature than Ni/CeO_2 catalyst.

Introduction and Motivations

It is well known that perovskite-type oxide catalysts (ABO_3) are highly active in complete oxidation reactions such as CO and PM oxidation. It has been reported that the catalytic activity can be greatly enhanced by substituting a part of the A-site metal ions with other metal ions. For example, partial substitution of Sr ions in $LaMnO_3$ improved the activity of propane oxidation[1]. In some cases, a valence change of metal ions occurs during the catalytic reaction; the Pd^{2+} ions are reported to exist at the lattice points of perovskite-type oxides in an oxidizing atmosphere and exit to the surface as metal in a reducing atmosphere. In this study, we focus on Ce ions, which have redox properties of +3/+4 depending on the oxygen partial pressure. This study reports a new preparation of $LaFeO_3$ catalysts with partial substitution of Ce ions and the reverse water gas shift reaction (RWGS reaction) using this catalyst.

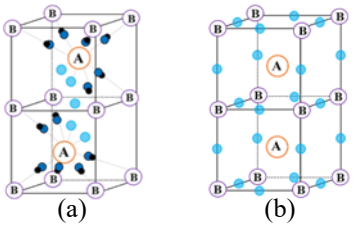


Figure 1. Structures of (a) heteronuclear metal cyano complex and (b) perovskite-type oxide

Materials and Methods

We have reported that ABO_3 catalyst can be prepared by thermal decomposition of heteronuclear cyano metal complex precursor (CN method)[2, 3]. This new method is expected to yield ABO_3 catalyst with high surface area and high homogeneity due to the similarity of precursor and product structures (Fig. 1). The heteronuclear metal cyano complexes, $AA'[B(CN)_6]\cdot nH_2O$ (A = lanthanide metal ion, A' = cerium ion, B = iron or cobalt ion), were prepared and calcined at 500-1000 °C to yield $A_{1-x}A'_xBO_3$ catalyst. The resulting catalysts were characterized by XRD, BET, H_2-TPR, XAFS (XAS), EIS, and ASR methods. The RWGS reaction was performed under the following reaction condition: CO_2 conc. = 2.5%, H_2 conc. = 10%, He balance, total flow rate = 100 cm^3min^{-1}, catalyst weight = 0.2 g). The product gas was analyzed by gas chromatography (TCD).

Results and Discussion

Figure 2 shows XRD patterns of $La_{1-x}Ce_x[Fe(CN)_6]\cdot nH_2O$ calcined at 700 °C for 1 h. Two sets of peaks assigned to perovskite-type structure ($0 \le x \le 0.3$) and fluorite-type structure ($0.15 \le x \le 0.30$) were observed. All XRD peaks due to the perovskite-type structure shifted to higher angles with increasing x. This means that the lattice constant of the perovskite-type oxide decreases with increasing x, suggesting that Ce ions are incorporated into the lattice of the perovskite-type oxide. Hereafter, $La_{1-x}Ce_x[Fe(CN)_6]\cdot nH_2O$ calcined at 700°C is denoted as $La_{1-x}Ce_xFeO_3(700)$, but the sample with more Ce ions contains CeO_2 other than perovskite-type oxides.

H_2-TPR measurements were conducted for $La_{1-x}Ce_x[Fe(CN)_6]\cdot nH_2O$ calcined at 700 °C for 1 h. The results are shown in Fig. 3. No reduction peak was observed for the sample with x = 0 ($LaFeO_3$) up to 900 °C. The reduction peaks of samples with 0.05 ≤ x ≤ 0.30 were observed in the temperature range of 200-500 °C. The intensity in reduction peak increased with increasing x, indicating that the reduction of sample was accelerated by Ce ion. The reduction peak of $La_{1-x}Ce_x[Fe(CN)_6]\cdot nH_2O$ (0.05 ≤ x ≤ 0.30) calcined at 700 °C was very similar to that $La_{1-x}Sr_xFeO_{3-\delta}$[4], suggesting that perovskite-type oxide partially substituted by Ce ion possesses the oxidation ability like that partially substituted by Sr ion. The result of X-ray absorption spectroscopy suggests that Ce ion exists as trivalent ion in bulk of perovskite-type oxide.

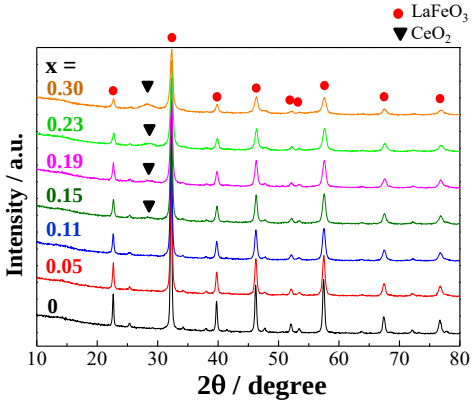


Figure 2. XRD patterns of $La_{1-x}Ce_x[Fe(CN)_6]\cdot nH_2O$ calcined at 700 °C for 1 h

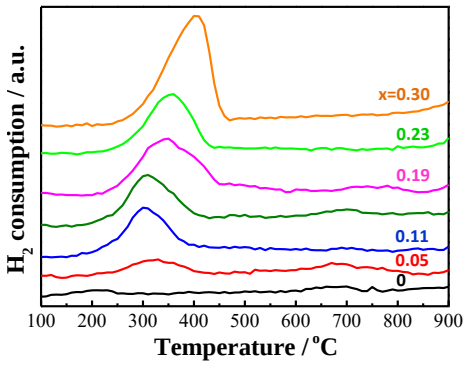


Figure 3. XRD patterns of $La_{1-x}Ce_x[Fe(CN)_6]\cdot nH_2O$ calcined at 700 °C for 1 h

Figure 4 shows the catalytic activity of $La_{1-x}Ce_xFeO_3$(700) for RWGS reaction. The Ni/CeO_2, catalyst[5] showed low activity below 400 °C. On the other hand, $LaFeO_3$ showed relatively high catalytic activity, and the catalytic activity was slightly enhanced by Ni addition. $La_{0.7}Ce_{0.3}FeO_3$(700) catalyst is not so active for RWGS reaction; however, its catalytic activity was extremely improved by the addition of Ni. It was found that the activity of $Ni/La_{0.7}Ce_{0.3}FeO_3$(700) catalyst was 10 times larger than that of Ni/CeO_2 catalyst (390 °C).

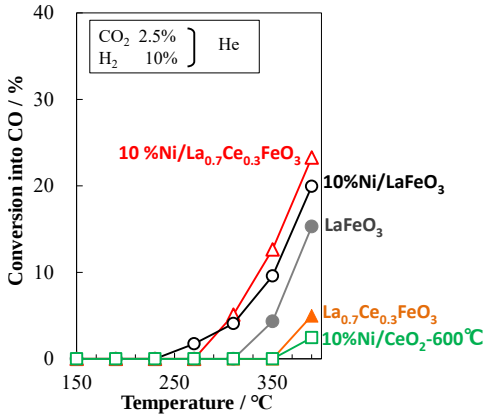


Figure 4. Catalytic activities for RWGS reaction over $La_{1-x}Ce_xFeO_3$(700) with and without Ni loading

References

1. T. Nitadori, S. Kurihara, M. Misono, *J. Catal.,* **1986**, *98*, 221.
2. M. Asamoto, H. Yahiro, *Catal. Surv. Asia* **2009**, *13*, 221.
3. M. Asamoto, M. Hino, S. Yamaguchi, H. Yahiro, *Catal. Today* **2011**, *175*, 534.
4. H. Chang, E. Bjørgum, O. Mihai, J. Yang, H. L. Lein, T. Grande, S. Raaen, Y.-A. Zhu, A. Holmen, D. Chen, *ACS Catal.* **2020**, *10*, 3707.
5. Y. Liu, Z. Li, H. Xu, Y. Han, *Catal. Cummun.* **2016**, *76*, 1.

Acknowledgements

The authors sincerely thank Prof. Nishibori (Tohoku University) for measuring X-ray absorption spectroscopy. This work was supported by JSPS KAKENHI Grant Number JP22K04831.

Oxygen migration and oxidation pathway for soot oxidation in presence of NO by two-step isotope experiment

Zirui Zhang[1,2], Cen Sun[1,2], Xiaolin Wei[1,2], Shaohua Wu[3], Gehan A J Amaratunga[4], , Feng Bin[1,2,*], Wenjun Liang[5]

[1] *State Key Laboratory of High-Temperature Gas Dynamics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China;*

[2] *School of Engineering Science, University of Chinese Academy of Sciences, Beijing 100049, China;*

[3] *Dalian University of Technology, Dalian 116000, PR China;*

[4] *Department of Engineering, University of Cambridge, CB3 0FA, Cambridge, United Kingdom;*

[5] *Key Laboratory of Beijing on Regional Air Pollution Control, Beijing University of Technology, Beijing 100124, PR China.*

** e-mail corresponding: binfeng@imech.ac.cn*

Significance and Relevance

NO plays a dual role in the NOx-assisted mechanism for soot oxidation. On one hand, NO facilitates oxidation by generating NO_2, a potent oxidant that reduces the overall oxidation temperature. On the other hand, NO competes with gas-phase oxygen for active sites on the catalyst, which can impede the oxidation rate. Thus, in the presence of NO, soot oxidation proceeds via two distinct pathways: a faster reaction involving direct interaction with lattice oxygen and a slower pathway where NO is first oxidized to NO_2 through a Langmuir-Hinshelwood mechanism before it participates in soot oxidation.

Preferred and 2nd choice for the topic: Automotive and stationary emission control and Fundamental advances in understanding catalysis

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Environmental pollution, especially the release of Particulate Matter (PM) such as soot and Nitrogen Oxides (NO_x), has gained significant attention recently. The primary issue has been obtaining NO_x-facilitated soot oxidation at moderate temperatures. The study of the oxidation mechanism of soot can lay a theoretical foundation for the development of high-performance catalysts.

Results and Discussion

To clarify NO_2's role in soot oxidation, we analyzed catalytic NO oxidation across all samples (**Fig.1A**), finding $CuCeO_x$ > CuO > CeO_2 in activity, with $CuCeO_x$ reaching 80% NO conversion at around 320 °C. In the primary soot oxidation range (250-500 °C), NO conversion remained high, with notable NO_2 presence. As temperature increased, NO converted to NO_2, reaching a peak level before decreasing in line with the thermodynamic equilibrium between NO and NO_2[1].

Temperature-Programmed Oxidation (TPO) tests on SO/PU oxidation showed that all catalysts reduced oxidation temperatures over a wide range (300-700 °C) (**Fig.1B**), ordered as $CuCeO_x$ > CuO > CeO_2. SO displayed a lower peak oxidation temperature than PU, attributed to more surface oxidizable functional groups. Each catalyst showed a narrow CO_2 peak, indicating complete oxidation. NO-TPO experiments further confirmed NO's role in lowering ignition temperatures and broadening CO_2 peaks, signifying its facilitative effect on oxidation. Soot from a diesel engine was also analyzed for oxidation characteristics. Compared to PU carbon, diesel soot had higher oxygen-functional groups (OFGs), enhancing its reactivity. TPO results showed CuCeOy to be most active (Tm = 352 °C in O_2/Ar, 342 °C in O_2+NO/Ar), likely due to Cu-[O] interactions boosting NO oxidation to NO_2.

While NO assists in soot oxidation, it also competes with oxygen for catalyst surface sites, slowing the overall rate. NO oxidation to NO_2 follows the slower Langmuir-Hinshelwood (LH) mechanism, which limits available reactive oxygen for soot oxidation. Though NO_2 lowers the temperature required, this slower pathway means an overall reduced reaction rate compared to direct oxidation by lattice oxygen.

IR experiments (**Fig.3C**) on CuCeOy revealed that NO lowered the temperature required to break down carbonates in the presence of oxygen, improving oxidation efficiency. Trends in nitrate and

carbonate transformation suggested a pathway for intermediate species involved in soot oxidation. Bidentate nitrite concentrations peaked at 100 °C, with NO_2 production highlighting soot oxidation's complex chemistry.

Surface oxygen species were studied via Soot-TPR (**Fig.1D**) analysis in an oxygen-limited Ar atmosphere. Two main temperature regimes corresponded to oxygen species (O_2^- at 320-625 °C, and O_2^- at >625 °C), indicating that CuO had the highest adsorbed oxygen, followed by CuCeOy. Both catalysts displayed three soot reduction peaks, attributed to chemisorbed oxygen desorption, lattice oxygen, and active oxygen migration. CuCeOy's high activity, despite not having the largest reduction peak, was likely due to the synergy between copper and cerium, enhancing reactive oxygen species (ROS) [2,3].

In isotope-switching experiments (**Fig.1E**), lattice oxygen's direct reaction with soot was confirmed. $^{18}O_2$ injections produced $C^{16}O^{16}O$, $C^{16}O^{18}O$, and $C^{18}O^{18}O$, showing that lattice oxygen participates actively in soot oxidation. CuCeOy had balanced CO_2 isotopes, indicating bulk-to-surface oxygen migration. A final experiment with NO revealed that competitive adsorption reduced $C^{16}O^{18}O$ and $C^{18}O_2$ production, slowing oxidation. The increase in $C^{16}O^{16}O$ suggested that nitrates from NO adsorption play a role in soot oxidation.

Based on these findings, we propose a mechanism for NO-assisted soot oxidation over CuCeOy (**Fig.1F**): (1) lattice oxygen directly oxidizes soot, with CeO_2 aiding oxygen migration, and (2) NO oxidizes on CuCeOy, producing NO_2 that facilitates soot oxidation. Oxygen migration in both pathways ensures continuous activity.

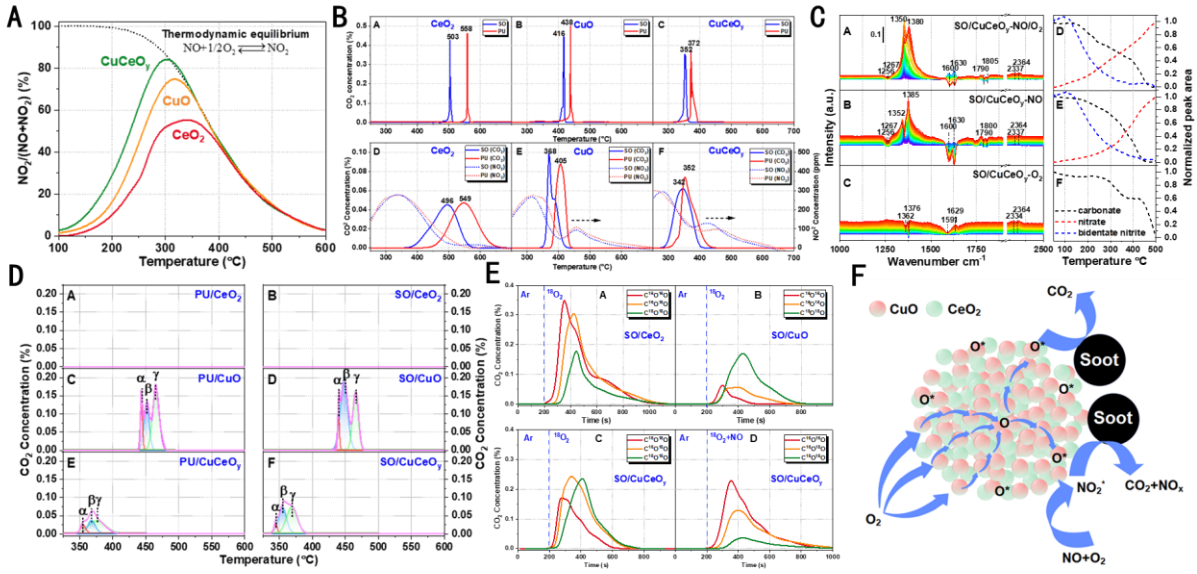


Figure 1 NO-TPO(A), Soot-TPO for SO/PU doped with CeO_2/CuO/$CuCeO_y$(B), IR spectra(C), Soot-TPR(D), instantaneous isotope switching experiment(E) and catalytic oxidation mechanism of soot particles by $CuCeO_y$ assisted with NOx(F).

References

1. A. Bueno-López, Diesel soot combustion ceria catalysts, *Applied Catalysis B: Environmental* **2014**, 146, 1–11.
2. P. Dulgheru, J.A. Sullivan, Rare Earth (La, Nd, Pr) Doped Ceria Zirconia Solid Solutions for Soot *Combustion, Top Catal* **2013**, 56, 504–510.
3. D. Mukherjee, B.G. Rao, B.M. Reddy, CO and soot oxidation activity of doped ceria: Influence of dopants, *Applied Catalysis B: Environmental* **2016**, 197, 105–115.

Acknowledgements

This work was supported by *National Natural Science Foundation Youth Fund (12302330, 52406171)* and *China National Postdoctoral Program for Innovative Talents (No. BX20230380).*

Design of Ceria-based Catalysts via Self-Combustion Approaches for CO_2 Conversion to Dimethyl Carbonate

Nicoletta RUSTA[1,2*], Valentina Mameli[1,2], Stefania Porcu[2,3], Aryane A. Marciniak[4], Evelyn C. S. Santos[5], Odivaldo Cambraia Alves [6], Claudio J. A. Mota[4,5,7], Elisabetta Rombi[1,2], Carla Cannas[1,2]

[1] *University of Cagliari, Department of Chemical and Geological Sciences, Cagliari, Italy.*
[2] *National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence, Italy.*
[3] *University of Cagliari, Department of Physics, , Cagliari, Italy.*
[4] *Universidade Federal do Rio de Janeiro, Escola de Química, Rio de Janeiro, Brasil*
[5] *Universidade Federal do Rio de Janeiro, Instituto de Química, Rio de Janeiro, Brasil*
[6] *Universidade Federal Fluminense, Instituto de Química, Niterói, Brazil*
[7] *INCT Energia & Ambiente, UFRJ, Brazil*
**n.rusta@studenti.unica.it*

Significance and Relevance

The sol-gel self-combustion synthesis (SC) or its combination with an impregnation strategy has allowed the obtaining of cerium oxide based catalysts used for the chemical conversion of CO_2 into dimethyl carbonate (DMC). The different structural and textural properties obtained allowed us to study the effect on the catalytic performance of nanoparticle shape anisometry in a case, and the homogeneous dispersion of the active phase on a mesostructured support with high surface area (SBA-15) in the other. These synthetic strategies are new to obtain catalysts for direct synthesis of DMC from CO_2 and methanol.

Preferred presentation: Oral only

Introduction and Motivations

At present, a key challenge in addressing greenhouse gas emissions is the development of technologies for capturing CO_2 and converting it into value-added products, a process known as Carbon Capture and Utilization (CCU). Among the various approaches, the direct synthesis of DMC offers a promising and sustainable method to convert CO_2 into a valuable eco-friendly solvent with applications in energy storage, such as lithium-ion batteries, and industrial chemistry: in dyes, pharmaceuticals and polycarbonates production. While various synthetic pathways exist for DMC production, many still rely on toxic and hazardous substances, such as phosgene, which poses significant health and environmental risks. This has driven research towards greener, more sustainable alternatives, with the direct synthesis from CO_2 and methanol emerging as the most attractive option. However, due to CO_2's kinetic inertness and thermodynamic stability, the process requires efficient catalysis. Ceria-based systems have emerged as particularly promising catalysts for this application, thanks to their chemical stability, redox properties, easy regenerability and storage under air conditions. In recent years, numerous synthetic methodologies have been used to obtain ceria systems having different morphologies, with the aim of increasing the defects and oxygen vacancies which are key parameters for improving their catalytic performance. For this reason, the self-combustion method (SC) was selected as it is fast (2-3 hours), green, scalable and allows to obtain platelet anisometric ceria nanoparticles. While, the combination of SC method with an impregnation strategy had the goal of reducing the amount of cerium used in the catalyst considering that it is a critical raw material and expensive.

Materials and Methods

Low porosity CeO_2 was prepared through SC synthesis and highly porous ordered CeO_2@SBA-15 nanocomposite was obtained by impregnation combined with SC method, with a final loading of 20

wt% CeO_2. In addition, as a reference, CeO_2 nanorods were prepared by hydrothermal synthesis (HT), the most promising systems proposed in the literature for the presence of oxygen vacancies due from their anisometric shape. The as-obtained catalysts were characterized using powder X-ray diffraction (XRD), Transmission electron microscopy (Conventional TEM, HRTEM, STEM-EDX), N_2-physisorption. In some cases, Raman spectroscopy, Electron paramagnetic resonance spectroscopy (EPR) and CO_2/NH_3 temperature-programmed desorption (CO_2/NH_3-TPD) measurements were performed. The direct synthesis of DMC was carried out in a batch reactor with a volume of 100 mL and GC-MS was used to evaluate the DMC formation.

Results and Discussion

The various synthetic strategies led to the obtainment of ceria-based systems with different microstructures and textures. More specifically, the following values of crystallite size and specific surface area were observed: ≈6 nm and 80 m^2/g for the CeO_2_SC sample, ≈8 nm and 622 m^2/g for the CeO_2@SBA-15 nanocomposite, ≈21 nm and 80 m^2/g for the CeO_2_HT sample. All catalysts showed catalytic activity for the direct synthesis of DMC. The CeO_2_SC sample showed a slightly higher DMC yield (1.6 $mmol_{DMC}\ g_{cat}^{-1}$) than the CeO_2@SBA-15 nanocomposite (1.4 $mmol_{DMC}\ g_{cat}^{-1}$), and the reference (CeO_2_HT), showed the best catalytic performances (3.8 $mmol_{DMC}\ g_{cat}^{-1}$). The better catalytic performances obtained of the CeO_2_HT sample compared to the CeO_2_SC catalyst are due to the fact that the CeO_2_HT sample has a higher concentration of oxygen vacancies and a lower concentration of strong basic sites. This result highlights how these key parameters have an important role in the direct synthesis of DMC. On the other hand, the CeO_2@SBA-15 nanocomposite showed the worse catalytic performance, due to its lower amount of active phase (20%). By normalizing the catalytic activity as a function of the active phase of the catalyst, however, it can be noticed how the CeO_2@SBA-15 composite shows the best performance (7.0 $mmol_{DMC}\ g_{act.ph.}^{-1}$) compared to the pure ceria samples, presumably due to the fine dispersion of the active phase throughout the mesostructured matrix, leading to a high exposed area of the active phase. This result highlights that the homogeneous dispersion of ceria on SBA-15 through proper impregnation strategy (CeO_2@SBA-15) could be a promising approach to design efficient catalysts. In addition, the effect of dehydrating agents is under study. In fact, the in *situ*-water removal due to the addition of dehydrating agents to the reaction involves the shift of the chemical equilibrium towards a greater conversion of methanol with a consequent increase in the yield of DMC.

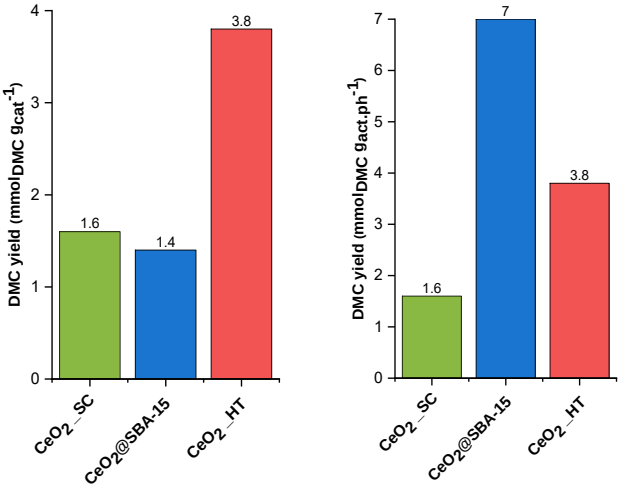


Figure 1. DMC yield (sx), DMC yield normalized as a function of active phase (dx)

Plasma-Driven Modulation of Metal-Organic Frameworks for CO2 hydrogenation

Nan Zou, Ying Zheng*
Western University, Dept. of Chemical and Biochemical Engineering
London, Ontario, Canada
** ying.zheng@uwo.ca*

Significance and Relevance

Achieving controllable pore structure design while preserving the original topology of metal-organic framework (MOF) materials remains a formidable challenge. In this study, we introduce a novel plasma-assisted radical etching (PRE) strategy to modulate the pore structure of HKUST-1 under ambient conditions. Utilizing OH* and CO* radicals as etchants, the PRE strategy enables tailored pore structure modulation through ligand substitution and the reduction of metal ion oxidation states, respectively. CO demonstrates the best reduction result. 80% Cu(II) was converted to Cu(I) within only 3 hours, and the MOF crystal structure is well preserved. The obtained Cu(I)-HKUST catalyst exhibited good selectivity of alcohols in the plasma-assisted CO_2 hydrogenation.

Preferred presentation: (Oral only)

Introduction and Motivations

Metal-organic frameworks (MOFs) are constructed via the self-assembly of metal ions (or clusters) and organic ligands, have attracted attention owing to their predictable and designable pore structures, excellent porosity, and diverse functionalities[1-3]. These characteristics make MOFs highly potential in various applications, such as gas storage, gas separation, catalysis, etc.[4-7]. However, most MOFs exhibit microporous structures with pore sizes less than 2 nm, which limits the entry of large molecules into the internal pores and therefore limits MOFs application in some cases[8-10]. Hence, there is a high expectation for the fabrication of MOFs with larger pore sizes.

Until now, various methods have been reported to modify the pore structures of MOFs, such as the extended ligand method[11, 12], templating method[13-15], acid/base etching method[16, 17], etc. The first two methods are performed during the MOF synthesis, which may lead to sacrifices in the stability of the MOF structure. The acid/base etching method allows larger pores to be generated while maintaining the original topological structure of MOFs, but it challenges the acid/base resistance of MOFs. Therefore, despite considerable efforts, the development of a facile method to fabricate hierarchical porous MOFs (HP-MOFs) remains a pronounced challenge.

This work proposes a systematic plasma-assisted active radicals etching (PRE) strategy capable of modulating the pore structure of HKUST-1 at room temperature and ambient pressure. The results demonstrate that hierarchical porous of HKUST was obtained with maintaining the original topological structure of HKUST-1. The reduced catalysts become effective in hydrogenating CO2 into ethanol.

Materials and Methods

Chemicals: Copper nitrate trihydrate, anhydrous ethanol 1,3,5-benzene tricarboxylic acid, N, N-dimethylformamide, were purchased from Sigma-Aldrich and used as they were.

Methods: HKUST-1 was synthesized according to the reported method[18]. The PRE strategy was operated at ~35°C and ambient pressure in a DBD reactor. 0.5 g HKUST-1 samples are filled in the inner tube while cooling water is circulated in the outer tube to maintain the temperature. Water vapor and CO are fed into the reactor and excited by plasma to OH^* and CO^* etchants. Operating conditions: 35°C, ambient pressure, 25 mL/min of etchants. The catalysts were evaluated in the same DBD reactor right after the catalyst reduction at is set at 30 mL/min with H_2: CO_2 = 3:1, maintained at 35 W for 2 hours.

Results and Discussion

XRD analysis (Fig. 1a) demonstrated the influence of the PRE strategy using OH^* as the etchant on the crystal structure of HKUST-1. Characteristic peaks corresponding to the {200}, {220}, and {222}

crystal planes are observed at 2θ = 6.5°, 9.5°, and 11.5°, respectively, indicating the successful synthesis of HKUST-1. After PRE treatment, the XRD patterns are in perfect agreement with those of the original HKUST-1, suggesting the maintenance of the characteristic topology structure of HKUST-1. The decreased peak intensity observed on the catalyst with prolong treatment time, 12 hours.

The pore size distribution curve (Fig. 1b) showed the pore structure of original and modulated catalysts. The untreated HKUST-1 has microporous structures with 7 Å and 8 Å pore sizes. With the increasing duration of PRE treatment, mesoporous structures began to appear on the HP-HKUST-n(OH*) samples, with a gradually increasing trend in mesopore sizes, thus confirming the effective modulation of the HKUST-1 pore structure using the PRE strategy. Unlike the PRE-OH* strategy, the PRE-CO* strategy does not achieve pore modulation by ligand substitution in the HKUST-1 coordination structure. Instead, it induces the spontaneous dissociation of ligands by reducing the oxidation state of copper ions to prepare HP-HKUST-n. As shown in Fig. 2c, the capacity of the PRE-CO* strategy to reduce the valence state of Cu^{2+} ions to Cu^{+}.

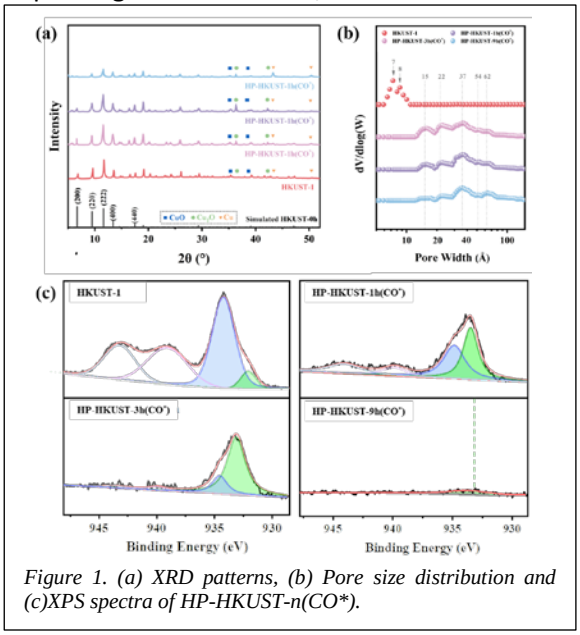


Figure 1. (a) XRD patterns, (b) Pore size distribution and (c)XPS spectra of HP-HKUST-n(CO).*

The PRE-CO* strategy demonstrates surprisingly high efficiency in reduction. 80% Cu(II) was converted to Cu(I) within only 3 hours, and the MOF crystal structure is well preserved. This reduced catalyst is continued to undergo CO2 hydrogenation reaction. About 33% CO_2 was converted in one throughput. The selectivity of ethanol reach 64.3% of the liquid products.

References

[1] J. Reboul, S. etc. Nature materials, 11 (2012) 717-723.
[2] H.-C. Zhou, etc. Chem. Rev. 2012, pp. 673-674.
[3] K. Shen, etc. Science, 359 (2018) 206-210.
[4] L. Song, J. etc. EES, 5 (2012) 7508-7520.
[5] Y. Chen, V. etc. Inorg. Chem., 51 (2012) 9156-9158.
[6] H. Wang, Q.-L. Zhu, R. Zou, Q. Xu, Chem, 2 (2017) 52-80.
[7] S. Peng, etc. Nat Commun, 9 (2018) 1293.
[8] W. Xuan, etc. Chem. Soc. Rev., 41 (2012) 1677-1695.
[9] I. Senkovska, etc., ChemComm, 50 (2014) 7089-7098.
[10] Z. Fang, etc. JACS, 136 (2014) 9627-9636.
[11] M. Eddaoudi, etc. Science, 295 (2002) 469-472.
[12] D.A. Gomez-Gualdron, etc. Chem. Mater, 26 (2014) 5632-5639.
[13] M.-H. Pham, etc. Cryst. Growth Des., 12 (2012) 1008-1013.
[14] L.G. Qiu, etc. Angew Chem, 120 (2008) 9629-9633.
[15] P. Rani, etc. Inorg. Chem. Frontiers, 5 (2018) 2856-2867.
[16] Y. Qin, etc. ACS Catalysis, 10 (2020) 5973-5978.
[17] J. Zhou, etc. Small, 16 (2020) 1906564.
[18] S.S.-Y. Chui, etc. Science, 283 (1999) 1148-1150.

Acknowledgements

The authors are grateful for the financial support provided by the Natural Sciences and Engineering Research Council of Canada

TiO_2 on Gold Nanostars Enhances Photocatalytic Water Reduction in the Near Infrared Regime

Camilla MONACCIANI, Debora Ferrari, Tiziano Dainese, Chiara Deriu, and Laura Fabris
Polythecnic of Turin, Department of Applied Science and Technology (DISAT), Corso Duca degli Abruzzi 24, Turin, Italy
camilla.monacciani@polito.it

Significance and Relevance

The synthesis of gold nanostars coated with a conformal layer of crystalline titanium dioxide (AuNS@TiO_2) through a simple hydrothermal route has enabled the photocatalytic evolution of hydrogen from water under solar illumination. The innovative combination of the photocatalyst's nanostar morphology, which generates a higher flux of hot electrons easily transferred through the thin TiO_2 tips, and the reversal of the coupling order of the two materials, with gold on the inside and the semiconductor on the outside, allowed solar radiation to be used up to the infrared portion of the spectrum to produce green hydrogen.[1]

***Preferred and 2nd choice for the topic*:** Photocatalysis and photoelectrocatalytic approaches, solar energy utilization; H_2 storage and transportation, green H_2 production, hydrogen vectors

***Preferred presentation*:** Oral preferred or Short Oral

Introduction and Motivations

Hydrogen, as an energy carrier, has emerged as one of the possible solutions to climate change, being an energy-rich substance that facilitates translocation and/or storage (in the form of gaseous, liquid, or solid H_2 or through chemicals) for the purpose of using it in a temporal and/or spatial context distinct from the original production site. Hence, there is the to find production routes that come from sustainable sources and at the same time are viable and industrially competitive.
In this scenario, heterogeneous photocatalysis enabled by nanoparticles in suspension emerges as one of the most promising processes. It does not require intermediate systems that generate energy, such as photovoltaic panels or wind turbines, and the surface area available for light absorption for the water splitting reaction is greater by not being fixed on a substrate.
TiO_2, while being the desirable semiconductor for these applications, due to its stability under reaction conditions, low cost, and proper alignment of valence and conduction bands, unfortunately has a wide band gap that limits its applicability mainly to UV irradiation conditions. However, by exploiting star-shaped plasmonic nanoparticles as promising additives to TiO_2, it is possible to extend the photocatalytic efficiency of the semiconductor into the visible and near-infrared (NIR) for hydrogen generation.

Materials and Methods

TiO_2 growth on gold nanostars was performed from titanium isopropoxide ($Ti(OCH(CH_3)_2)_4$ as the precursor in a non-aqueous environment (isopropanol). Acetic acid was added to the growth solution to control TiO_2 growth. Next, crystallization occurred by heat treatment of AuNS@TiO_2 particles in isopropanol at a temperature of 70°C for two days. The solution was washed with 1:1 MilliQ water and ethanol mixture and then dried to produce a powder. Photocatalytic activity of the samples was tested via batch-phase water reduction with methanol as a sacrificial agent. The as-produced AuNS@TiO_2 catalyst was dispersed in 10 mL of reaction solution via sonication. The reactor was illuminated by a 150-W xenon ozone-free arc lamp (Newport). Magnetic stirring was employed to ensure that the AuNS@TiO_2 remained suspended in the reaction medium. The hydrogen production rate was monitored of the reactor headspace gas into the thermal conductivity detector of a GC (Agilent 7890B).

Results and Discussion

By epitaxially growing a conformal shell of crystalline TiO_2 on the nanostructures via a low-temperature hydrothermal protocol, a defect- and strain-free interface between gold nanoparticles and TiO_2 is generated. This unencumbered morphology allows plasmonically generated hot electrons to be more easily transferred across the Schottky barrier between the Fermi level of the metal (Au) and the conduction band of the semiconductor (TiO_2). Furthermore, the intimate contact between metal and semiconductor allows for more efficient light absorption and subsequent hydrogen production than conventional approaches that deposit metal clusters on TiO_2. *(Figure 1)*

The high potential of this new nanomaterial led to the birth of the StarLIGH_2T technology. A project based on the patented catalyst just described can make the most of the solar spectrum, absorbing more than 90 percent of the radiation, far exceeding the limitations of conventional photocatalysts, which are only able to utilize a small fraction of the entire solar radiation.

StarligH$_2$t revolutionizes the state of the art in photocatalysis with this innovative photocatalyst capable of producing seven times more hydrogen than the commercial P25 TiO_2 photocatalyst. This figure highlights a major breakthrough over existing technologies, representing a concrete and highly competitive alternative for photocatalysis aimed at hydrogen production.

Figure 1

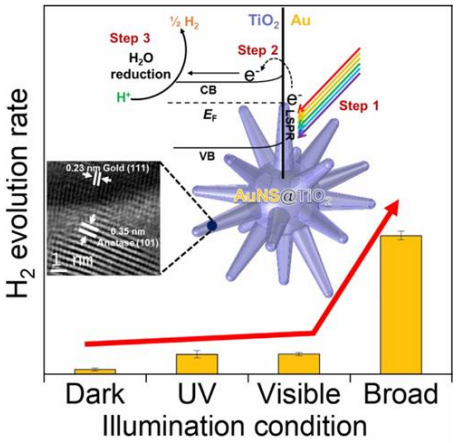


Figure 1 *Broad-spectrum light illuminates the TiO_2 coated gold nanostar (step 1). While shorter wavelengths interact with the TiO_2 band gap and the gold transverse LSPR band, longer wavelengths (800 nm) excite the longitudinal LSPR band of gold nanostars. The hot electrons at the nanostar tips overcome the Schottky barrier at the clean interface between the two materials and transfer into the conduction band of the TiO_2 semiconductor (step 2). Conduction band electrons then reduce protons and evolve hydrogen (step 3).*

References

1. Atta, S.; Pennington, A. M.; Celik, F. E.; Fabris, L. TiO_2 on Gold Nanostars Enhances Photocatalytic Water Reduction in the Near-Infrared Regime. *Chem.* **2018**, *4*, 2140– 2153, DOI: 10.1016/j.chempr.2018.06.004

Acknowledgements

We would like to thank Cassa Depositi e Prestiti (CDP) and the first National Technology Transfer Hub for Sustainability, Tech4Planet, for their support with an investment that has enabled StarLIGH_2T to be currently at Proof of Concept status.

INNOVATIVE METAL FUNCTIONALIZED HYDROXYAPATITE/CARBON NITRIDE NANOCOMPOSITE MATERIAL TO ENHANCE CO_2 ELECTROREDUCTION TO FORMATE

Michele BIGICA,[1] Sebastiano CAMPISI,[1] Antonella GERVASINI,[1] Pierangela CRISTANI,[2] Andrei KHODAKOV,[3] Vitaly ORDOMSKY[3]

[1] Dipartimento di Chimica, Università degli Studi di Milano, 20133 Milano, Italy
[2] Ricerca sul Sistema Energetico - RSE S.p.A., 20134 Milano, Italy
[3] CNRS-UCCS, 59650 Villeneuve d'Ascq Cedex, France
** michele.bigica@unimi.it*

Significance and Relevance

This study introduces novel and functional materials for producing value-added compounds via the electrochemical reduction of CO_2 (CO_2-ER). Furthermore, recent findings highlight hydroxyapatite ($Ca_5(PO_4)_3OH$, HAP) as a key modifier able to shift the product distribution[1], directing CO_2ER selectivity towards formate production[2]. We present here, efficient electrocatalysts based on metal onto carbon nitride-hydroxyapatite (CN-HAP) composites. These advanced materials exhibit exceptional performance in CO_2-ER, underscoring their significant potential for CO_2 conversion technologies.

Preferred and 2nd choice for the topic: 1) CO_2 utilization and recycling 2) Advanced process with electrocatalysis and plasma utilization.
Preferred presentation: Oral preferred

Introduction and Motivations

CO_2 as low-cost and abundant carbon resource can be used to produce high-value chemicals or fuel of high energy density: selective CO_2 electrochemical reduction is one of the most technologically and challenging pathways for carbon dioxide conversion. However, decreasing overpotential and enhancing both current density and faradaic efficiency (FE) remain a significant challenge, particularly in aqueous media, due to the competitive presence of hydrogen evolution reaction (HER). In this work, innovative nanocomposites comprising graphitic carbon nitride (CN), and decorated with copper (Cu) or bismuth (Bi) nanoparticles, along with hydroxyapatite (HAP) nanorods, were explored as electrocatalysts for CO_2 reduction to formate.

Materials and Methods

Composite preparation consisted of one-pot synthesis of a covalent organic framework of melamine followed by thermal annealing under inert condition[3] (Fig. 1). Structural, morphological and surface properties of composites have been characterized by XRF, XPS, XRD and HRTEM.

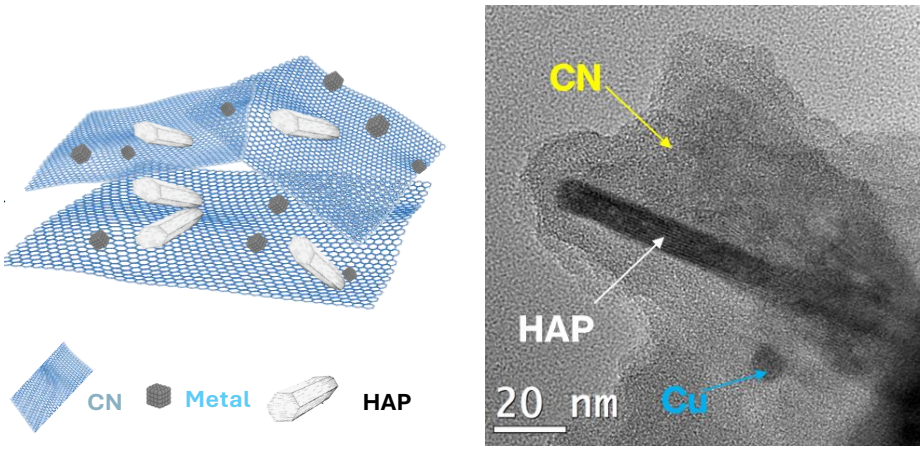


Figure 1 Schematic representation of hydroxyapatite-carbon nitride composite material functionalized with metal nanoparticles (left), Representative HRTEM images of the HAP_Cu@CN catalyst (right).

The performance of the electrocatalysts with copper and bismuth in CO_2-ER were evaluated and carried out using a three-electrode cell in a 0.1 M $KHCO_3$ aqueous solution.

Results and Discussion

Chronoamperometric tests at different applied potentials revealed that the metal-doped HAP-based catalysts facilitate CO_2ER at lower overpotentials, attributed to the synergistic effect of

hydroxyapatite and metal active sites. Linear sweep voltammetry curves (LSV) showed that admixing with HAP resulted in a slight increase in system activity as the current delivered is higher in the ternary composite material. Despite the inevitable presence of the parasitic hydrogen evolution reaction (HER), the composite materials show CO_2ER activity. Notably, both catalysts achieved high Faradaic efficiencies for formic acid: 60% for Cu and 85% for Bi at an applied voltage of -1.0 V (*vs* RHE), with moderate current densities of 120 and 75 mA cm^{-2}, respectively (Fig. 2).

The catalytic behavior varied between the metals: Bi-based catalysts showed a higher preference for producing formate, whereas Cu-based catalysts exhibited greater current densities, leading to improved overall CO_2 conversion. Both HAP_Cu@CN and HAP_Bi@CN catalysts outperformed their unmodified binary counterparts, Bi@CN and Cu@CN, which lacked HAP. This indicates that incorporating HAP significantly enhances the activity for CO_2 electroreduction. Current investigations are focused on understanding the role of HAP, particularly its interactions with $CO_{2(aq)}$ and HCO_3^-, which are recognized as key species in the CO_2 reduction reaction.

In summary, both composite materials demonstrated encouraging CO_2 conversion rates, indicating that integrating various surfaces, such as inorganic modifiers, can lead to the development of more effective and selective electrocatalysts. These findings pave the way for future research into optimizing composite catalysts for CO_2ER to achieve higher efficiency and product selectivity.

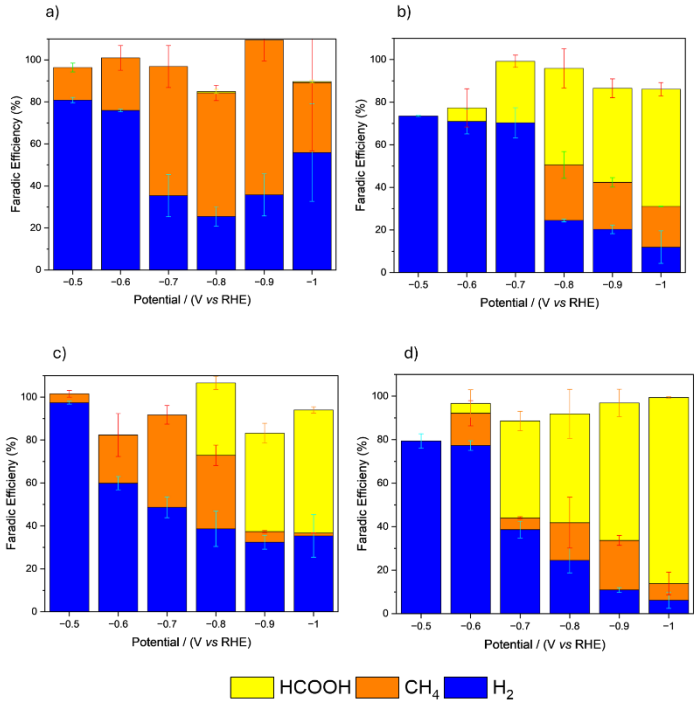


Figure 2 Faradic Efficiency (FE) and total current density on a) Cu@CN, b) Bi@CN, c) HAP_Cu@CN, d) HAP_Bi@CN in CO_2 saturated 0.1 M $KHCO_3$ solution for chronoamperometric catalytic test (1 h, RT).

References

1. Bigica, M.; Ghiara, G.; Cristiani, P.; Campisi, S.; Gervasini, A. Interface Properties of Hydroxyapatite in Ternary Composites Cathodes for Electromethanogenesis. *New Journal of Chemistry* **2024**, *48* (22), 9909–9919. https://doi.org/10.1039/D4NJ01053A.
2. Jiao, J.; Kang, X.; Yang, J.; Jia, S.; Peng, Y.; Liu, S.; Chen, C.; Xing, X.; He, M.; Wu, H.; Han, B. Steering the Reaction Pathway of CO2 Electroreduction by Tuning the Coordination Number of Copper Catalysts. *J Am Chem Soc* **2024**, *146*, 15917–15925. https://doi.org/10.1021/JACS.4C02607/ASSET/IMAGES/LARGE/JA4C02607_0005.JPEG.
3. Gao, T.; Kumar, K. S.; Yan, Z.; Marinova, M.; Trentesaux, M.; Amin, M. A.; Szunerits, S.; Zhou, Y.; Martin-Diaconescu, V.; Paul, S.; Boukherroub, R.; Ordomsky, V. Covalent Organic Framework Derived Synthesis of Ru Embedded in Carbon Nitride for Hydrogen and Oxygen Evolution Reactions. *J Mater Chem A Mater* **2023**, *11* (36), 19338–19348. https://doi.org/10.1039/D3TA01362F.

Acknowledgments

This work has been financed by the Research Fund for the Italian Electrical System under the Contract Agreement between RSE S.p.A. and the Ministry of Economic Development - General Directorate for the Electricity Market, Renewable Energy and Energy Efficiency, Nuclear Energy in compliance with the Decree of April 16th, 2018.

Direct hydrogenation of CO_2 into liquid hydrocarbons: kinetics and reactor design

Antoinette MAARAWI CHIDRAOUI*[,1], Carlotta PANZONE[1], Alban CHAPPAZ[1], Geneviève GEFFRAYE[1], Albin CHAISE[1]

[1]*Univ Grenoble Alpes, CEA, Liten, DTCH, Laboratoire Réacteurs et Procédés (LRP), 38000 Grenoble, France.*

** antoinette.maarawi@cea.fr*

Significance and Relevance

This study aims to develop a new reactor technology for the direct CO_2 hydrogenation into sustainable aviation fuels. At first, a kinetic study is conducted by testing an iron-based catalyst under various conditions. The obtained "α" values are within the range of values generally obtained for traditional CO-FT processes. Then, the analysis of extensive experimental results has led to the development of a kinetic model, which is integrated in a reactor model. Based on these findings, a novel millistructured reactor design is proposed, with promising 3D simulation results.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling, Sustainable and clean energy production and transport
Preferred presentation: Oral preferred.

Introduction and Motivations

The direct hydrogenation of CO_2 to hydrocarbons (HC) via the Fischer-Tropsch (FT) process is a versatile method for producing various gaseous and liquid hydrocarbons. This approach combines the reverse water-gas shift (RWGS) reaction and FT synthesis in a single reactor, commonly using iron-based catalysts due to their dual activity. While advancements in catalyst development exist, reaction kinetics are often overlooked. Our group recently published data on a Fe-K/Al_2O_3 catalyst and developed a macro-kinetic model for producing linear alkanes, 1-alkenes and alcohols with up to 20 carbon atoms[1]. This study seeks to test Fe-K supported catalyst, refine the kinetic model and examine reactor design impacts.

Materials and Methods

Our experimental work consists on testing a Fe-K supported iron catalyst in a fixed-bed tubular reactor (10.2 mm inner diameter, 210 mm total length) under different conditions in order to develop reaction kinetics model (using Matlab). Prior to each test, the catalyst undergoes in-situ reduction at 310°C for 24 hours under H_2/N_2 flow. Non-condensed gases and liquid products are analyzed using an online µ-GC system and an offline GC-MS system, respectively. The effects of several operating parameters are investigated: temperature (250 – 300°C), total pressure (10 – 20 bars), H_2/CO_2 ratio (3 – 12) and τ_{mod} defined as the catalyst mass divided by the total inlet gas volume flow (0.36 – 1.33 $g \cdot s \cdot Nml^{-1}$). Two- and three-dimensional (2D/3D) fixed-bed reactor models that incorporate the kinetic model of the FT-CO_2 reaction are developed using COMSOL Multiphysics.

Results and Discussion

For all the tests, the calculated total mass and carbon balances are very satisfactory (<15% error), confirming the high accuracy of the analyses of the gaseous, aqueous and organic phases resulting from the reaction. The results in figure 1 show that increasing the contact time of the gases with the catalyst, increases CO_2 conversion (X_CO_2) from 25% to 35%, decreases CO selectivity (S_CO) from 32% to 10% and enhances the production of C_{5+} hydrocarbons by 7 to 10%. This means that the FT reaction is limiting and the conversion of CO to HC is favored. In addition, we found that HC are secondary products of the reaction and CO is formed first. The results also showed that increasing temperature favors X_CO_2, since the equilibrium of the RWGS reaction is shifted towards CO formation. Temperature favors dissociation of the CO formed, which decreases S_CO. Olefin production is enhanced (olefin/paraffin ratio increases); however, very little effect of temperature is observed on C_{5+} selectivity. Increasing H_2/CO_2 ratio results in an increase of CH_4 production and a decrease in C_{2+}

hydrocarbon production due to excess of H_2 which promotes the hydrogenation of CO to CH_4. When increasing the total pressure from 10 to 20 bars, X_CO_2 is increased by 10% and S_CO selectiviy decreases by 50%. Above 15 bars, CH_4 production is stable but an increase in C_{2+} hydrocarbons is observed, which encourages to operate the reaction at at least 15 bars. On the other hand, the results showed an effect of adding CO at the inlet of the reactor on the HC distribution, due to competitive adsorption between CO and CO_2 where CO wins (X_CO_2 decreases and X_CO increases when increasing the molar fraction of CO at the reactor inlet).

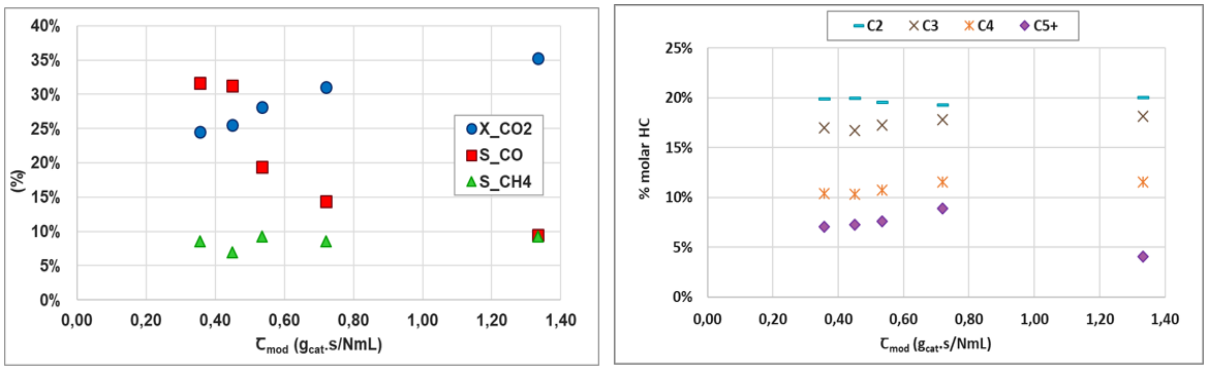


Figure 1: a) CO_2 conversion and CO selectivity b) mole fraction of hydrocarbons vs contact time.

To describe the distribution of hydrocarbons obtained as products during FT synthesis, an important parameter is the probability α of chain growth of the hydrocarbon formed. By correlating the experimental data, an α between 0.70 - 0.73 is obtained. This is a very interesting result, since these α values are within the range of values generally obtained for traditional CO-FT processes (α = 0.7 - 0.8 for CO-FT processes between 250-350°C for iron-based catalysts[2]).

Based on these obtained data, the kinetic model proposed in our previous work[1] is adjusted and integrated in the reactor model. This latter is able to describe with good accuracy the CO_2 conversion and CO selectivity, as well as hydrocarbons distribution according to their C number and their chemical nature. In the simulations as in the experiments, thermal profiles show a temperature rise (ΔT) of up to 15°C in the catalytic bed in the tubular reactor, potentially influencing selectivity for long-chain hydrocarbons[3]. To mitigate this, a structured reactor is designed and assessed via 3D simulations, showing a reduced ΔT of under 1°C while maintaining comparable performances to the tubular reactor. An optimized reactor design is proposed which allows sustaining performance with doubled production (g/h) and an acceptable ΔT (3°C). Although promising, further investigations are necessary. Sensitivity analyses are conducted by varying geometric parameters of the reactor to enhance efficiency in FT-CO_2 synthesis.

In conclusion, while significant progress has been made in developing catalysts for direct CO_2 hydrogenation, the influence of reactor design on performance has yet to be explored. This study aims to bridge this gap by presenting an innovative reactor technology specifically adapted for enhancing CO_2 valorization and process intensification.

References

1. C. Panzone, R. Philippe, C. Nikitine, L. Vanoye, A. Bengaouer, A. Chappaz, P. Fongarland, *Ind. Eng. Chem. Res.* **2021**, *60*, 16635−16652.
2. Chai et al., *Catalysts* **2023**, *13*, 1052.
3. R. Philippe, M. Lacroix, L. Dreibine, C. Pham-Huu , D. Edouard, S. Savin, F. Luck, D. Schweich, *Catal. Today*. **2009**, *147S*, S305-S312

CO_2 Sorption Accelerated by Mechanical Grinding.

Maria Rosaria ACOCELLA *[1], Aida KIANI[2] Katerina KOSTANTINOVA CHARAKOVA[1]
[1]*University of Salerno, Department of Chemistry and Biology "A Zambelli", Via Giovanni Paolo II, 132-84080-Fisciano (Salerno)*
** e-mail corresponding: macocella@unisa.it*

Significance and Relevance

The most widely used CO_2 capture technologies are based on adsorption technology. Although the use of amine solutions is a commercially successful technology, an attractive alternative is solid adsorption processes. Solid-state reactions of alkylamine to carbamate have been already investigated, but the kinetic of the reaction is slow at room temperature for ambient CO_2 reaching full conversion only after 1000 h. In this study the kinetics of conversion of the amine to ammonium-carbamate in ambient CO_2 is strongly accelerated by ball milling with full conversion achieved after only 4h.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling ; Green chemistry and biomass transformation, renewable resources conversion
Preferred presentation: (Oral only)

Introduction and Motivations

The reaction of ammonia with CO_2 to give ammonium carbamate is a well-known process,[1] which in the last two decades was proposed as a process for CO_2 capture.[2] The most widely employed sorbents for CO_2 capture are aqueous solutions of organic amines, (mainly mono ethanolamine), which can selectively form alkylammonium carbamates.[3]
Solid-state reactions of alkylamine surfactants to ammonium carbamates were thoroughly investigated by Belman and coworkers, also showing the relevance of this reaction to nanocrystal synthesis.[4] These studies showed complete alkylammonium carbamate formation, which is also fast for high CO_2 concentrations. However, the kinetics of carbamate formations are slow at room temperature for ambient CO_2. The aim of this work is to explore the ability of mechanochemistry to accelerate the CO_2 capture from ambient air by a crystalline alkylamine surfactant.

Materials and Methods

Octadecylamine (ODA) was purchased by by Sigma Aldrich and used without any further purification. Conversion of ODA to the corresponding carbamate (OAOC), in different conditions, was studied by four different techniques: WAXD, FTIR, TGA, and DSC

Results and Discussion

This study explores possible procedures to accelerate CO_2 capture from ambient air by a crystalline alkylamine surfactant (ODA), leading to the corresponding crystalline ammonium-carbamate. Kinetics of reactions of crystalline ODA with CO_2, leading to OAOC, can be easily obtained by DSC scans, by evaluating melting enthalpies of residual ODA. The kinetics of conversion of the amine to ammonium-carbamate in ambient CO_2 is strongly accelerated by ball milling with full conversion achieved after only 4h, while the reaction kinetics of ODA powder simply exposed to ambient CO_2 is much slower, with full conversion only after nearly 1000h. A substantial increase in kinetics of the solid-state ODA reaction with ambient CO_2 can be also achieved by increasing the temperature up to 50°C, However, the time for full conversion remains much higher than for room temperature ball-milled ODA powder (roughly 100h vs 4h). It is apparent that ball-milling is an effective procedure to accelerate the reaction of solid amines with low-concentration CO_2.

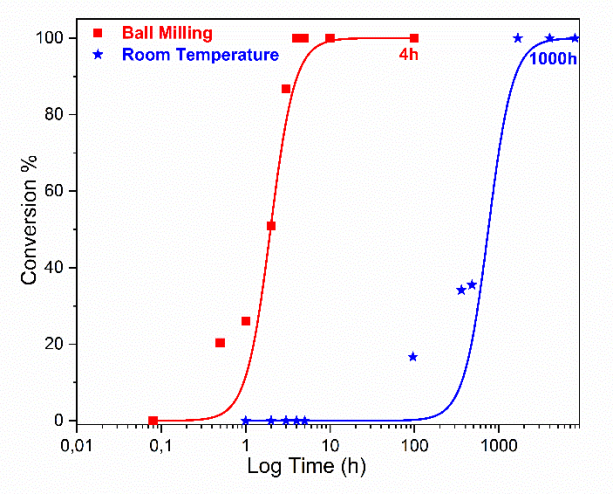


Figure 1 . Kinetics of reactions of crystalline ODA with CO_2 leading to OAOC, as evaluated by DSC scans, from melting enthalpies of residual ODA. All reactions are with ambient CO2: Red line and squares by exposure to air at room temperature; blu line and stars by ball-milling at 100 rpm at room temperature.

References

1. L. A. Brooks, L. F. Audrieta, H. Bluestone and W. C. Jofinsox, in Inorganic Syntheses, John Wiley & Sons, Ltd, **1946**, pp.85–86.
2. F. Barzagli, F. Mani, M. Peruzzini, Green Chem. **2011**, 13, 1267–1274.
3. J. R. Switzer, A. L. Ethier, E. C. Hart, K. M. Flack, A. C. Rumple, J. C. Donaldson, A. T. Bembry, O. M. Scott, E. J. Biddinger, M. Talreja, M. Song, P. Pollet, C. A. Eckert, C. L. Liotta, ChemSusChem **2014**, 7, 299–307.
4. N. Belman, J. N. Israelachvili, Y. Li, C. R. Safinya, J. Bernstein, Y. Golan, J. Am. Chem. Soc. **2009**, 131, 9107–9113.

Acknowledgements

Financial support of Ministero dell'Università e della Ricerca (MUR) is acknowledged.

Integrated direct air capture and activation of CO_2 on metal-free covalent triazine frameworks

Fabian H. Müller[1], Chalachew Mebrahtu[1,2], Regina Palkovits[*1,2]

[1] *Institute for Technical and Macromolecular Chemistry, RWTH Aachen University, Worringerweg 2, 52074 – Aachen, Germany.*

[2] *Institute for Sustainable Hydrogen Economy, Forschungszentrum Jülich, Am Brainergy Park 1, 52428 – Jülich, Germany.*

**palkovits@itmc.rwth-aachen.de*

Significance and Relevance

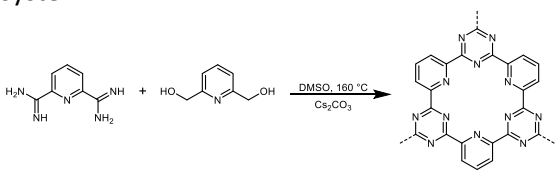
We present a novel process, that couples carbon dioxide capture from ambient air (direct air capture: DAC) with subsequent thermocatalytic CO_2-activation to carbon monoxide over a dual-functional, metal-free covalent triazine framework (CTF). The herein presented integrated approach combining CO_2- capture & -utilization is, to the best of our knowledge, the first system of its kind to achieve DAC and metal-free, thermocatalytic CO_2 conversion over one dual-functional material.

Introduction and Motivations

Mitigating the impact of CO_2-emissions on our planet's environment constitutes one major challenge in the 21st century. Within the diverse field of mitigating measures, carbon capture constitutes one key technology. Established carbon capture technologies are predominantly solution-based, entailing high energy-demand for solvent regeneration.[1] In addition, solvent-based systems are not optimized for DAC conditions and are difficult to couple within an integrated carbon capture and utilization process (ICCU).[1] Accordingly, research focus shifted towards solid sorbent materials, for example, covalent triazine frameworks (CTFs).[2, 3] The application of solid sorbents enables the possibility to elegantly circumvent the inherent uncertainty of underground CO_2-storage by valorizing the inexpensive C_1-building block carbon dioxide *via* CO_2-conversion. Hereby, the innovative ICCU approach not only mitigates the impact of CO_2-emissions, but enables the flexible, decentralized and cost-efficient production of platform chemicals.

Materials and Methods

The used CTF in this work, 2,6-pyridine-CTF (2,6-py), was synthesized *via* polycondensation of 2,6-pyridinediamidine and 2,6-pyridinedimethanol (Scheme 1). After workup, the CTF was calcined at 300 °C for 4 h. Structural integrity was confirmed *via* ^{13}C solid-state NMR spectroscopy, infrared spectroscopy, x-ray diffraction and N_2-physisorption. Framework stability until 300 °C was confirmed by TGA-MS and TPR under H_2-atmosphere. ICP-OES analysis confirmed the elemental composition and the absence of metals in the system.



Scheme 1: Polycondensation of 2,6-pyridinediamidine and 2,6-pyridinedimethanol to 2,6-pyridine-CTF.

ICCU-experiments consisted of two phases, CO_2 adsorption and CO_2 conversion. The former was conducted statically under a standard laboratory atmosphere for 12 h to recreate realistic DAC conditions. The adsorbent was subsequently transferred to a fixed-bed continuous gas-phase reactor. After loading, the reactor was flushed with Ar (100 mL min^{-1}, 3 h) to flush out loosely adsorbed species before it was pressurized to 20 bars (50/50 v/v H_2/Ar). Under the same gas composition, the temperature was ramped in 50 °C-steps between 100 °C and 300 °C while the reactor outlet was monitored by mass spectrometry for increased time resolution.

Results and Discussion

Preliminary gas adsorption studies on five different CTF structures revealed superior CO_2-uptake at low CO_2 partial pressures on 2,6-py (1.43 mmol CO_2 g^{-1} at p/p_o = 0.1) while N_2-physisorption confirmed

a well-developed pore structure with a BET-surface area of 476 m^2 g^{-1}. As high CO_2 affinity at low CO_2-concentrations is desirable for DAC-applications, 2,6-py was ICCU experiments (Figure 1).

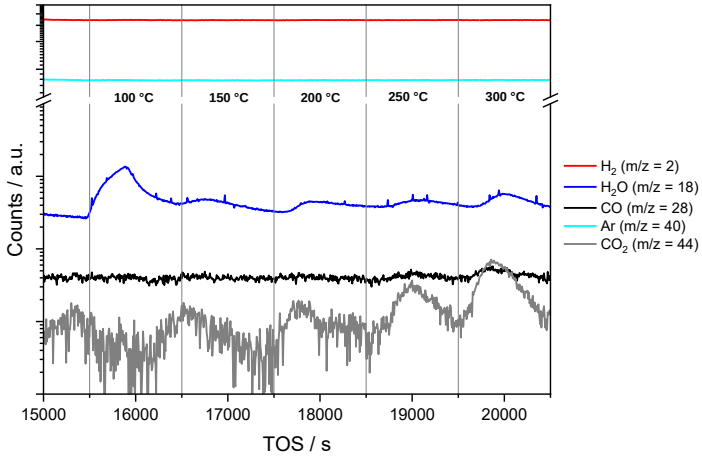


Figure 1: Mass spectra for mass-to-charge ratios (m/z) 2, 16, 18, 28, 40, and 44 for an ICCU experiment on 400 mg 2,6-py. T = 100-300 °C, 20 bar, total flow = 100 mL min^{-1} (50/50 v/v H_2/Ar).

ICCU-experiments consist of an adsorption, a flushing and a conversion phase. For clarity, figure 1 only displays the CO_2-conversion phase. At 100 °C, the desorption of water (m/z = 18) and physisorbed CO_2 (m/z = 44) is observed. A temperature increase to 150 °C triggers another minor water desorption. Starting from 200 °C, chemisorbed CO_2 is desorbed increasingly with increased temperature. Simultaneously, m/z = 18 (H_2O) and 28 (CO) were increased. High-temperature water desorption and decomposition of the framework or synthesis artefacts were excluded through thorough preliminary tests. Hence, CO_2, CO and H_2O between 200 and 300 °C indicate an intrinsic activation of CO_2 to CO according to water-gas shift equilibrium (Scheme 2).[4] This behavior was qualitatively reproducible over 5 cycles with the same catalyst batch as well as with different batches of the 2,6-py-CTF.

$$CO_{2\,(g)} + H_{2\,(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$$

Scheme 2: Water-gas shift equilibrium.[4]

To confirm the intrinsic activation of adsorbed CO_2 to CO, the reactor outlet gas stream at 250 °C was sampled and analyzed *via* gas chromatography. Besides H_2, Ar and CO_2, carbon monoxide could be confirmed in the outlet gas stream. In addition, 2,6-py was tested under CO_2 hydrogenation conditions (250 °C, 20 bars, H_2/CO_2 3:1) and displayed consistent CO_2 conversion (< 0.5 %) to CO for 24 h.
In conclusion, a metal-free 2,6-py-CTF was employed in a novel ICCU-process. This system combines true DAC with coupled conversion of the adsorbed CO_2 to CO in a solvent-free system, thereby enabling a cost-efficient and highly flexible solution to simultaneously combat CO_2-emissions while valorizing CO_2 as C_1-building block for platform chemicals.

References

1. M. Yusuf, H. Ibrahim, *J. Environ. Chem. Eng.* **2023**, 11, 111393.
2. Z. Zhou, T. Ma, H. Zhang, S. Chheda, H. Li, K. Wang, S. Ehrling, R. Giovine, C. Li, A. H. Akawadhi, M. M. Abduljawad, M. O. Alawad, L. Gagliardi, J. Sauer. O. M. Yagi, *Nat.* **2024**, *635*, 96.
3. G. Tuci, A. Iemhoff, A. Rossin, D. Yakhvarov, M. Gatto, R. Balderas-Xicohtencatl, L. Zhang, M. Hirscher, R. Palkovits, C. Pham-Huu, G. Giambastiani, *Int. J. Hydrog. Energy* **2022**, 47, 8434.
4. Y. He, F. H. Müller, R. Palkovits, F. Zeng, C. Mebrahtu, *Appl. Catal., B* **2024**, *345*, 123663.

Acknowledgements

We gratefully acknowledge funding by the Cluster of Excellence Fuel Science Center (EXC 2186, ID: 390919832) funded by the Excellence Initiative by the German federal government to promote science and research at German universities.

Dry Reforming of Biogas over $La_{0.9}Sr_{0.1}Fe_{0.95}Ni_{0.05}O_3$ Perovskite for Syngas Production

María ROMAY [1], David P. SERRANO[1,2], José.M ESCOLA[2], Patricia PIZARRO[*,2]

[1] *Thermochemical Processes Unit, IMDEA Energy Institute, Avda. Ramón de la Sagra 3, Móstoles, 28935 Madrid, Spain.*

[2] *Chemical and Environmental Engineering Group, Rey Juan Carlos University, c/ Tulipán s/n, Móstoles, 28933 Madrid, Spain.*

** patricia.pizarro@imdea.org*

Significance and Relevance

The presented research addresses the primary challenges associated with the dry reforming of biogas for syngas production, a pivotal process for sustainable industrial applications. The effect of reaction temperature and simulated biogas composition is studied using a previously optimized $La_{0.9}Sr_{0.1}Fe_{0.95}Ni_{0.05}O_3$ perovskite as catalyst and oxygen carrier. Advanced characterization techniques revealed exsolution of Ni nanoparticles and higher amounts of oxygen vacancies than the Ni-free perovskite, which account for its high activity and H_2/CO ratios of 1 under certain conditions. Impurities of water and O_2, however, led to significant changes in H_2/CO ratio. Finally, its application in chemical looping DRM denoted a remarkable stability after 50 cycles.

Introduction and Motivations

Dry reforming (DR) is recognized as one of the most cost-effective technologies for simultaneously capturing CO_2 and converting CH_4 into valuable syngas (CO+H_2). A promising strategy for conducting DR is chemical looping mediated by solid oxygen carriers, which involves alternating reduction and oxidation steps. During the reduction step, the oxide releases oxygen, and it is subsequently regenerated in the oxidation step[1]. Perovskite-type catalysts are particularly well-suited for DR due to their high thermal stability and exceptional oxygen mobility[2].

This study introduces an innovative approach to DR by implementing the chemical looping process using an enhanced perovskite composition ($La_{0.9}Sr_{0.1}Fe_{0.95}Ni_{0.05}O_3$)[3], assessing its stability and catalytic activity over 50 cycles of alternating reduction and reoxidation with CO_2. In addition, tests were carried out to simulate the composition of biogas by adding oxygen, water or both molecules to the feed. Furthermore, it provides a novel methodology for optimizing processes involving complex compositions, such as biogas, through applying linear programming (LP) as an analytical tool to identify competing reactions.

Materials and Methods

The $La_{0.9}Sr_{0.1}Fe_{0.95}Ni_{0.05}O_3$ perovskite was prepared using a modified Pechini method. The catalytic tests were carried out in a vertical fixed-bed reactor coupled to a Mass Spectrometer. Isothermal reactions were run at three temperatures (800, 850 and 900 °C) and co-feeding different CH_4/CO_2 ratios with a constant WHSV of 6000 L/(kg.h). The effect of impurities was evaluated performing reactions at 900°C using different proportions of water and oxygen. Redox cycles were performed at 900 °C: a DR stage (25 min co-feeding CH_4/CO_2=1.5/1) was alternated with an oxidation step (feeding CO_2 for 5 min), in total 50 cycles were accomplished. The structure of the perovskites before and after reaction was determined by XRD and the chemical mapping of the catalysts was carried out employing SEM technique. XPS spectra were acquired to check the different oxygen states in the perovskite before and after reaction. Elemental analysis was carried out to determine the amount of carbon deposited on the perovskite after reaction. The extent of the simultaneous reactions occurring during the catalytic tests was evaluated using linear programming (LP) optimization.

Results and Discussion

The impact of reaction temperature was first assessed during the reduction step using the $La_{0.9}Sr_{0.1}Fe_{0.95}Ni_{0.05}O_3$ perovskite at 800, 850, and 900 °C for 3 h with a CH_4/CO_2 ratio of 1.5:1, similar to biogas composition. Higher temperatures significantly enhanced CH_4 and CO_2 conversions and brought the H_2/CO ratio closer to 1, highlighting the dominance of the DR reaction. Remarkably, no catalyst deactivation was observed throughout the process. SEM analysis of the post-reaction sample revealed the formation of small (40–50 nm) spherical Ni-rich particles exsoluted on the perovskite surface. It is

also remarkable that a greater quantity of oxygen vacancies, associated with higher O donation and CO_2 activation capacity, were observed in the O1s XPS spectra of this particular perovskite.

Given the superior performance at 900 °C, this temperature was chosen to study feed composition. Lowering the CH_4 proportion boosted the conversion of both CH_4 and CO_2, with the H_2/CO ratio stabilizing around 1, reaffirming the DR reaction's prevalence. In contrast, introducing only CH_4 shifted the process toward methane decomposition, significantly compromising the perovskite's stability. Linear programming (LP) optimization was used to identify the dominant reactions at different stages of isothermal tests conducted at 900 °C for the $La_{0.9}Sr_{0.1}Fe_{0.95}Ni_{0.05}O_3$ perovskite. This approach provided insights into how the composition of the perovskite influences the extent of the reactions that take place. Moreover, tests were conducted by adding oxygen and water, similar amounts to those in a biogas, to the feed. Results showed minimal impact on CH_4 and CO_2 conversions, but with a slight increase in hydrogen production during steam reforming and lower H_2/CO in the case of O_2 addition.

Finally, after 50 redox cycles, the perovskite's effectiveness in chemical looping DRM (CL-DRM) was validated alternating DRM and CO_2 regeneration. CH_4 and CO_2 conversions slightly decreased to 84.3% and 93.6% (Figure 1), respectively, which is an outstanding result. Notably, the H_2/CO ratio, stayed consistently within the 1.0–1.1 range throughout the experiment, confirming the sustained dominance of the dry reforming of methane (DRM) reaction over the 50 cycles. This approach demonstrates strong potential for maintaining the performance of an optimized Ni-perovskite in long-term DRM process.

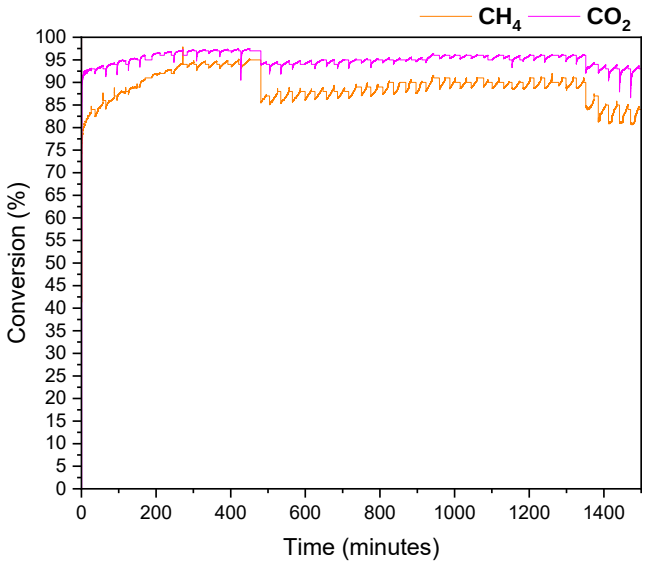


Figure 1. CH_4 and CO_2 conversions of the 50 redox cycles carried out with the $La_{0.9}Sr_{0.1}Fe_{0.95}Ni_{0.05}O_3$ perovskite.

In summary, higher temperatures in the range from 800 to 900 ºC affords greater conversions and H_2/CO ratios closer to 1, enhancing the efficiency of the DR reaction. Co-feeding CO_2 with CH_4 is pivotal to sustain DR dominance and protect the perovskite's structure. The introduction of oxygen and water impurities has negligible impact on the conversions in DR process, but modifies the H_2/CO ratio. Additionally, the cycling process demonstrates the perovskite's prolonged stability and activity after 50 cycles, confirming its significant potential for chemical looping dry reforming (CL-DR).

References

1. S. Bhattar, Md. A. Abedin, S. Kanitkar, J. J. Spivey, *Catal. Today*, **2022,** *365*, 2.
2. J.Zhang, H.Wang, A.K. Dalai, *Ind. Eng. Chem. Res.*, **2009**, *48*, 2, 677-684.
3. M. Romay, D.P. Serrano, J.M. Escola, P. Pizarro, Chem. Eng. **2024**, 496, 154039.

Acknowledgements

The authors acknowledge financial support from Comunidad de Madrid (CM MICINN) through the project HUBS / MADRID + CIRCULAR and from from the Ministry of Science and Innovation through the project HYWARE (PID2021-124705OB-I00).

Effective conversion of CO_2 at lower temperatures in an electric field

Yasushi SEKINE*,1
[1]Waseda University, Department of Applied Chemistry, Shinjuku, Tokyo, Japan.
* ysekine@waseda.jp

Significance and Relevance

We investigated the reverse water–gas shift (RWGS) reaction using an electric field at temperatures below 473 K. Highly dispersed $Ru/ZrTiO_4$ catalysts with 2 nm particles exhibited high RWGS activity, while larger Ru particles favored CO_2 methanation. The electric field enhanced hydrogen migration, maintaining high CO selectivity and preventing CO hydrogenation into CH_4. Reaction mechanisms were explored through various techniques, including *in-situ* DRIFTS, providing insights into the low-temperature RWGS process.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling and *Catalysis to electrify the chemical promotion*
Preferred presentation: *Oral only*

Introduction and Motivations

Many countries are aiming to reduce CO_2 emissions to near zero, and catalytic CO_2 conversion with green hydrogen is a key focus. The reverse water–gas shift (RWGS) reaction, which produces carbon monoxide (CO), plays a central role in converting CO_2 into value-added chemicals. However, RWGS is endothermic and requires high temperatures for significant conversion. Recent studies have explored unconventional methods like electrocatalysis to enable CO_2 conversion at milder conditions. Applying an electric field to semiconductor-catalysts can enhance reactions by promoting proton migration, and opening new reaction pathways. This work investigates the use of electric fields for efficient, low-temperature RWGS on highly dispersed Ru catalysts.

Materials and Methods

The catalysts were prepared using a complex polymerization method with citric acid, ethylene glycol, and metal precursors, followed by calcination. Ruthenium (Ru) nanoparticles were synthesized *via* colloidal reduction with ethylene glycol and then mixed with supports. Activity tests were conducted in a fixed-bed reactor with an electric field applied across the catalyst bed, monitoring gas compositions by GC. Catalysts were characterized using ICP-OES, FE-TEM, XAFS, H_2-TPR, and *in-situ* DRIFTS to analyze Ru loading, particle size, electronic states, and catalytic behavior. The electric field enhanced selectivity and activity for CO formation, with reaction conditions evaluated through various testing parameters such as temperature, H_2/CO_2 ratio, and contact time.

Results and Discussion

We investigated the use of Ru-supported catalysts for the reverse water-gas shift (RWGS) reaction in an electric field, comparing two preparation methods for 1.5wt% Ru-supported catalysts: a Ru-colloid supporting method and an impregnation method. The colloidal Ru catalyst exhibited superior performance, achieving 95.9% selectivity for RWGS, compared to only 24.7% for the impregnated catalyst, alongside better Ru dispersion and smaller particle size (2.37 nm vs. 7.97 nm). The colloidal Ru catalyst was selected for further tests, as it showed better performance in the RWGS reaction, particularly in an electric field.

The application of an electric field enhanced the RWGS reaction at lower temperatures (as low as 423 K), where conventional RWGS showed no activity. The electric field reduced the apparent activation energy to 6.74 kJ/mol, significantly lower than the 64.5 kJ/mol observed without the field. Additionally, CO_2 conversion increased proportionally to the applied current, while CO selectivity remained high (>90%), suggesting that the electric field promotes the reaction through a different mechanism.

Stability tests revealed that the catalytic activity without the electric field decreased with time course, while the activity in the electric field remained stable at any temperature. The electric field also helped in regenerating activity by purging with hydrogen, which removed CO_2-derived adsorbates. Further tests showed that in the electric field, high selectivity for RWGS was maintained even in H_2-rich conditions, where conventional systems tend to favour methane (CH_4) formation. The electric field suppressed side reactions like CO_2 methanation and maintained high CO selectivity even at longer contact times.

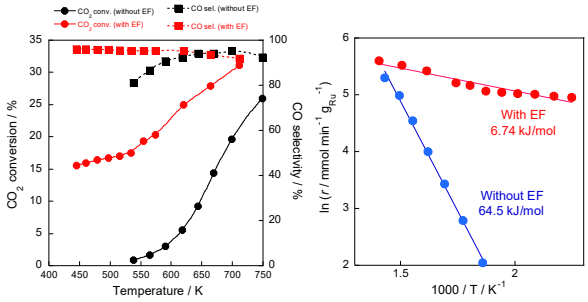


Figure 1 Activities (left) and Arrhenius plots (right) for the RWGS reaction over the $Ru/ZrTiO_4$ catalyst in and without the electric field; CO_2: H_2: Ar = 1: 1: 2; total 100 SCCM; 100 mg catalyst; 0 or 5.0 mA input current.

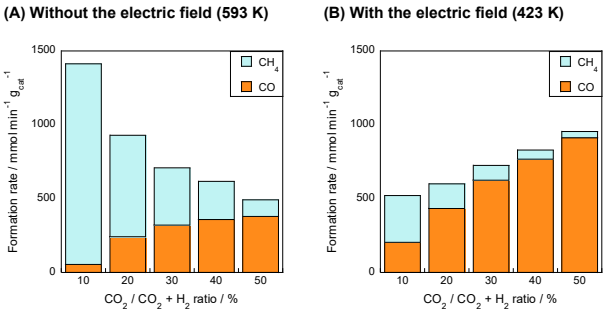


Figure 2 CO and CH_4 formation rate over the $Ru/ZrTiO_4$ catalyst under various H_2/CO_2 ratios (A)without the electric field at 593 K and (B)in the electric field at 423 K; 100 SCCM total flow rate; 100 mg catalyst weight.

The proposed mechanism suggests that the electric field promotes hydrogen migration from the Ru surface to the support, enhancing the formation of oxygen vacancies on the metal oxide support. These vacancies help activate CO_2, leading to more efficient CO formation and reduced byproduct formation (e.g., CH_4). *In-situ* DRIFTS measurements revealed that the electric field altered surface species, decreasing the intensity of formate species and increasing the formation of CO and more reactive intermediates, such as carboxylate and carbonate species.

This study shows that highly dispersed ruthenium (Ru) catalysts have high reverse water-gas shift (RWGS) activity in an electric field, even at low temperatures where conventional methods are inactive. These catalysts achieve high CO selectivity, especially under high H_2 concentrations or short contact times, thanks to fast hydrogen migration. The electric field shifts the reaction from a formate-mediated path to a redox mechanism, enhancing both hydrogen spillover and CO_2 activation, resulting in improved low-temperature RWGS activity and selectivity.

References

1. Y. Sekine *et al., EES Catal.*, 1, 125-133, 2023.
2. Y. Sekine *et al., RSC Adv.*, 12, 9036-9043, 2022.
3. Y. Sekine *et al., Chem. Commun.*, 57, 5737-5749, 2021.
4. Y. Sekine *et al., Faraday Discuss.*, 229, 341-358, 2021.

Acknowledgements

A part of this work was supported by JSPS KAKENHI (grant no. 23H05404 and 23K20034) from the Japan Society for the Promotion of Science.

How to improve stability in excess-methane dry reforming over Ni/KIT-6 catalysts? Reduction behavior of thermally stable Ni phyllosilicates (Si/Ni=1:1) monitored by *in situ*/*operando* XAS-XRD and IR spectroscopy

Katarzyna ŚWIRK DA COSTA[1], Paulina SUMMA[2], Marco FABBIANI[3], Magnus RØNNING[1]
[1]*Norwegian University of Science and Technology, Department of Chemical Engineering, 7491 Trondheim,Norway*
[2]*Sorbonne Université, CNRS, Institut Jean Le Rond d'Alembert, 78210 Saint Cyr l'Ecole, France*
[3]*Université de Caen, ENSICAEN, CNRS, Laboratoire Catalyse et Spectrochimie, 14000 Caen, France*
** katarzyna.swirk@ntnu.no*

Significance and Relevance

Synthesis gas is one of the most important intermediates to produce chemicals and fuels. For the first time, excess-methane dry reforming was studied over a Ni/KIT-6 catalyst synthesized by one-pot method. This method allowed Ni phyllosilicate to form *in situ* within the silica framework. As monitored by *operando* XAS-XRD, Ni phyllosilicate (Ni/Si=1:1) was found to be thermally stable after reduction at 750°C for 90 min (4% H_2/He) and during the catalytic test (CH_4/CO_2/Ar=5.3/3.0/1.7, 700°C). The catalyst showed remarkably stable catalytic behavior compared to an impregnated sample. More dispersed Ni species contributed to improved stability with less coke formation.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling, Sustainable and clean energy production and transport
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster) Oral only

Introduction and Motivations

Dry (CO_2) reforming of methane (DRM) has emerged as the most widely studied reaction to convert CH_4 and CO_2 into synthesis gas[1]. The synthesis gas is a versatile feedstock used for production of methanol and synthetic fuels. Excess-methane dry reforming poses an alternative to the conventional DRM as it can offer a future choice for upgrading low-quality natural gas to synthesis gas.

DRM has been widely investigated over nickel-based catalysts due to their high activity and relatively low cost compared to noble metals, yet, their performance may be limited due to sintering of nickel and carbon build-up[1]. KIT-6 mesoporous silica has a unique 3D channel network, allowing easy access of host species without blocking the pores. Ni/KIT-6 silica catalysts are commonly prepared through post-synthesis impregnation of the silica support with an aqueous Ni solution, however, even at low loading (ca. 5 wt.%) nickel particles can be deposited on the outer surface of silica, reducing the strength of their interaction with support[2]. A pH adjustment strategy appears as one of the most efficient solutions, allowing Ni species to be introduced during one-pot synthesis method.

Metal phyllosilicates have attracted attention in catalysis research due to their unique lamellar structure offering strong metal-support interaction (MSI), and small metal domain size having high dispersion[3]. In the existing literature, Ni phyllosilicate (Ni-PS) formation is not addressed in the context of KIT-6. The pH value can significantly affect the formation of 1:1 Ni-PS by polycondensation between $Ni^{2+}(OH)_2$ and silicic acid Si–OH on the SiO_2 framework. Moreover, as far as we surveyed, the nature of Ni-PS 1:1 as well as their role in excess-methane dry reforming were not previously studied. Herein, we aim at understanding the behavior of Ni-PS supported on KIT-6-like silica using *in situ* or *operando* techniques: X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD), and IR spectroscopy.

Materials and Methods

KIT-6/Ni onepot, KIT-6/Ni imp catalysts and parent supports (KIT-6 pH9, KIT-6) were studied. The one-pot synthesis assumed preparation steps typical for KIT-6 synthesis protocol[4] with some modifications. After addition of Pluronic P123 (4g), HCl (7.47g), $Ni(NO_3)_2{\cdot}6H_2O$ (0.061 mol), TEOS (8.6g) and aging for 20h, the pH of the solution was adjusted to 9 by dropwise addition of ammonia solution (25%). The hydrothermal synthesis was carried out at 100°C for 24h. The sample was dried and calcined at 600°C for 6h. KIT-6 support was also synthesized at pH of 9, excluding the addition of nickel precursor. For the sake of comparison, KIT-6/Ni imp was synthesized by wet impregnation as described elsewhere[4]. By combining a variety of characterization methods (ICP-OES, N_2 physisorption, SAXS, TPR-H_2, HRTEM, H_2 chemisorption), we examined the role of Ni phyllosilicates in KIT-6-like mesoporous

silica. The catalytic tests were carried in $CH_4/CO_2/Ar$ = 53/30/17 and WHSV = 120,000 $ml \cdot h^{-1} \cdot g_{cat}^{-1}$. *In situ/operando* XAS-XRD were performed at the SNBL (BM31) at ESRF, France. XAS scans were collected during reduction in 4%H_2/He (*in situ*) and excess-methane dry reforming (*operando*) at the Ni K-edge, while collecting XRD patterns. The reaction flow was monitored by MS. *In situ* IR spectroscopy of CO adsorption was performed at room temperature to characterize the Ni sites.

Results and Discussion

ICP-OES analysis showed that both catalysts had similar content of Ni: 6.0 wt.% (KIT-6/Ni onepot), 6.2 wt.% (KIT-6/Ni imp). *In situ* XAS-XRD revealed that KIT-6/Ni imp showed typical transformation of NiO to Ni^0, whereas diffraction peaks of $Ni_3Si_2O_5(OH)_4$, posing a structure of nepouite (Ni/Si 1:1) were observed for KIT-6/Ni onepot. As illustrated in Fig. 1a,b, nickel phyllosilicate (Ni-PS) partially reduced to metallic phase, while a certain content of Ni species retained their initial cationic state. According to TPR-H_2, the degree of reduction was 75.9% for onepot sample, while the impregnated material was reduced close to 100%. Excess-methane dry reforming was conducted over the reduced catalysts. The KIT-6/Ni onepot showed remarkably stable CO_2 and CH_4 conversions, as well as H_2/CO molar ratio, whereas KIT-6/Ni imp exhibited a declining trend (Fig. 1c,d). *Operando* XAS-XRD experiments revealed that Ni oxidation state did not change for both catalysts which indicates that the catalyst deactivation is due to carbon formation instead of a rapid oxidation (Fig. 1e-h). *Operando* XRD showed that the mixture of Ni phyllosilicate and Ni^0 was stable under reaction conditions (Fig. 1g). No increase in crystallite size was registered for Ni^0 retaining 6.5±0.2nm for KIT-6/Ni onepot, and 10.3±0.1nm for KIT-6/Ni imp. For the latter, the intensity of the graphite peak increased over time.

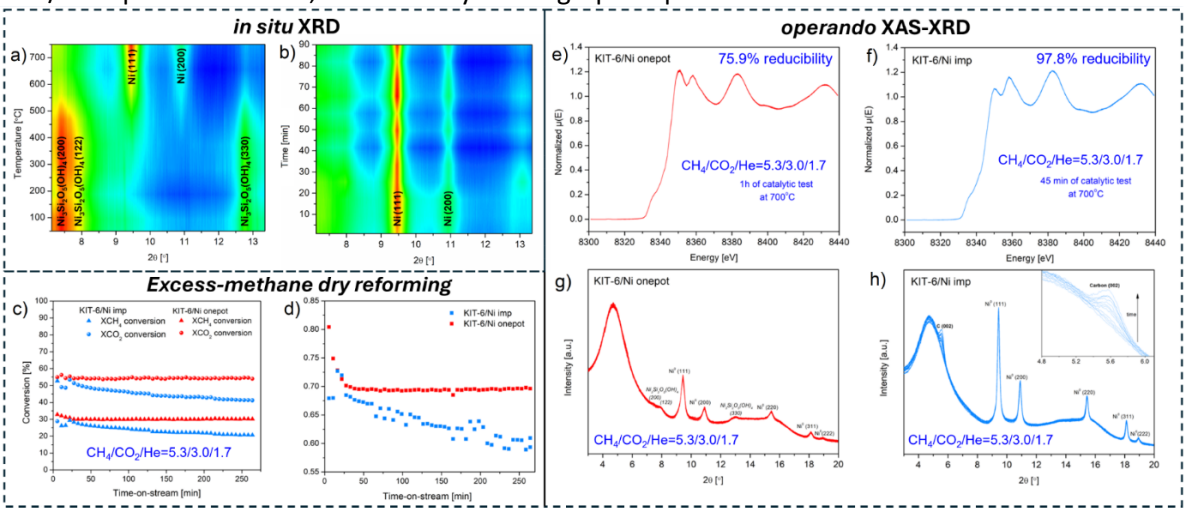


Figure 1 Contour plots of the acquired *in situ* XRD (λ = 0.0338 nm): (a) KIT-6/Ni onepot during reduction as a function of temperature and time, (b) followed by isothermal reduction for 90 min. Catalytic tests in excess-methane dry reforming over KIT-6/Ni onepot and KIT-6/Ni imp, (c) CH_4 and CO_2 conversions, (d) H_2/CO molar ratio as a function of time-on-stream. *Operando* XAS-XRD changes registered during catalytic tests (e, f, g, h).

Our work provides insight into the impact of synthesis protocols on KIT-6-supported Ni sites and how stability can be tuned to improve DRM. Further optimization of our synthesis promises to push the boundaries of catalyst stability for excess-methane dry reforming.

References

1. D. Pakhare and J. Spivey, *Chem. Soc. Rev.*. **2014**, *43*, 7813.
2. O. Daoura *et al.*, *Appl. Catal. B Environ.* **2021**, *280*, 119417.
3. S. Kuhaudomlap *et al.*, *ACS Omega*. **2022**, *8*, 249.
4. K. Świrk Da Costa *et al.*, *Energy Fuels*. **2023**. *37*, 18952.

Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie Grant agreement No 892571. The BM31 setup at ESRF was funded by the Swiss National Science Foundation (grant 206021_189629) and the Research Council of Norway (grant 296087). The data presented are from proposal 31-01165.

A scalable artificial leaf device with high solar-to-fuel efficiency to formate

Daniele GIUSI[*,1], Veronica COSTANTINO[1], Viviana AMOROSO[1], Sefora Isabella PERRICONE[1], Siglinda PERATHONER[1], Gabriele CENTI[1], Claudio AMPELLI[1]

[1] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences (ChiBioFarAm) – University of Messina, ERIC aisbl and CASPE/INSTM, V.le F.Stagno d'Alcontres, 31 – 98166 Messina, Italy.*

** dgiusi@unime.it*

Significance and Relevance

This study presents the development of a scalable artificial leaf-type device that integrates a photovoltaic module (PV) with an electrochemical cell (EC) to convert carbon dioxide (CO_2) into valuable chemicals using solar radiation.[1] The research focuses on the successful synthesis and optimization of a CuBi-based gas-diffusion electrode, which demonstrates outstanding performance in reducing CO_2 to formate. A solar-to-fuel (STF) efficiency of 8.3 % is achieved at a current density of 17 mA cm^{-2}, rising to around 10% also including the co-production of green hydrogen, which is one the highest STF efficiencies reported in the literature. Formate is a promising liquid energy carrier working under ambient conditions, showing potential as a hydrogen carrier in the emerging hydrogen economy. Additionally, this study highlights the role of surface engineering in enhancing electrode properties, such as hydrophilicity and double-layer capacitance, which are crucial to boost performance in CO_2 electrocatalytic reduction powered by solar energy and to scale the artificial leaf prototype for practical applications.[2]

Preferred topic and 2nd choice for the topic: Photocatalysis and photoelectrocatalytic approaches, solar energy utilization; CO_2 utilization and recycling
Preferred presentation: Oral preferred or Short Oral / Poster

Introduction and Motivations

An artificial leaf is an innovative technology that mimics natural photosynthesis to convert CO_2 into valuable fuels and chemicals using solar energy. This approach offers a sustainable solution for reducing greenhouse gas emissions and generating useful products for industry. The development of efficient and stable electrocatalytic materials/electrodes is crucial for optimizing the performance of photo-electrochemical (PEC) reactors and enabling their scalability. In this work, we developed a highly efficient copper-bismuth (Cu-Bi)-based electrocatalyst with exceptional selectivity to formate production and excellent stability, maintaining strong performance over ten hours of continuous operation. The PEC reactor used for the electrocatalytic tests was designed in a compact configuration to be easily scaled-up and to achieve industrially relevant current densities. The design focused on minimizing ohmic losses and optimizing internal gas and liquid flow pathways and incorporating electrodes with larger catalytic surface area than those typically reported in the literature, thereby enhancing its potential for scale-up operations.

Materials and Methods

The artificial leaf consists of i) a mini-PV module with four silicon heterojunction solar cells and ii) an advanced compact electrochemical cell (EC) made of Plexiglas (Figure 1a). The EC is equipped with a gas chamber for continuous CO_2 supply and operates under illumination from a solar simulator calibrated to provide certified 1 Sun (100 mW cm^{-2}). The Cu-Bi electrocatalytic material was synthesized through a simple hydrothermal method, and the final electrodes (with geometrical active area of around 5-10 cm^2) were prepared by depositing the resulting Cu-Bi powder onto gas-diffusion layers (GDLs) via spray-coating technique.

Results and Discussion

The artificial cell was validated in two consecutive 5-hour tests to evaluate both performance and stability. Interestingly, during the second 5-hour test, a substantial improvement in the Faradaic

selectivity to formate was observed, reaching a maximum of around 80%. The STF efficiency was calculated as 8.3 %, with the remaining part referred to green H_2 production and minorly to carbon monoxide (CO) formation. This STF value is among the highest reported in the literature, when combined with the achieved current density of 17 mA cm^{-2} and cell voltage of 2.5 V. The increasing performance during the second 5-hour test was attributed to the electrochemical activation of the catalyst. To prove this, three further consecutive chronoamperometries were performed at an applied voltage of - 1.2 V, achieving an increase in formate production at the expense of hydrogen (Figure 1b). Advanced *in situ* operando characterization revealed that this improvement was due to the reduction of Cu and Bi species, accompanied by an increase in the hydrophilicity of the catalyst.

Further investigations on the electrode's surface wettability demonstrated that optimizing the physical properties of the electrocatalyst, such as by varying synthesis parameters to enhance hydrophobicity, is critical for addressing selectivity in CO_2 conversion, beyond the nature of the electrocatalytic material itself. Under optimised conditions, a shift in process selectivity from a selective C1 pathway to C2+ products was observed. This can be achieved by modulating hydrogen accessibility through adjustments to the wettability properties of the electrode, opening new routes for designing highly efficient catalysts for CO_2 electrocatalytic reduction.

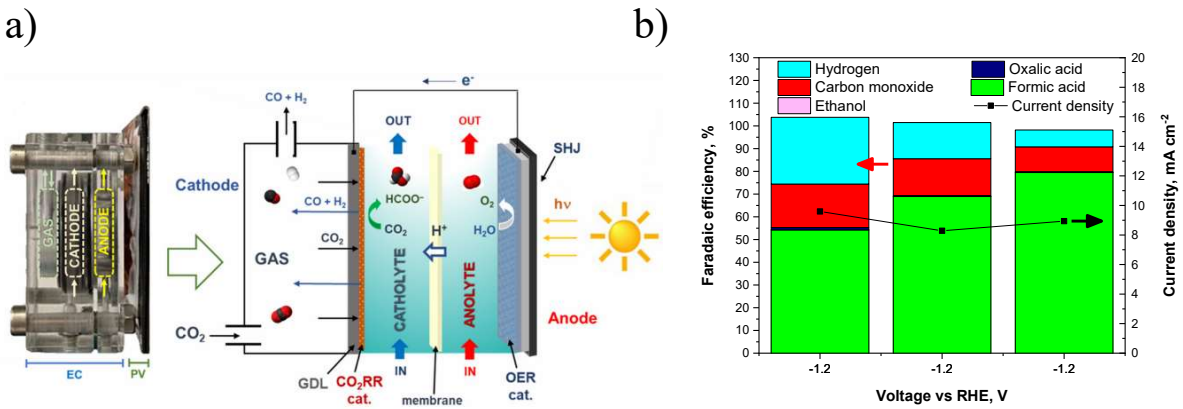


Figure 1. a) Picture and representative scheme of the artificial leaf for the selective formation of formate by CO_2 reduction b*)* Faradaic efficiency observed for the CuBi-based electrodes, showing the electrochemical activation of the catalyst during three consecutive chronoamperometries at the same applied potential (-1.2 V vs RHE).

References

1. C. Ampelli, D. Giusi, M. Miceli, T. Merdzhanova, V. Smirnov, U. Chime, O. Astakhov, A.J. Martín, F.L.P. Veenstra, F.A. Garcés Pineda, J. González-Cobos, M. García-Tecedor, S. Giménez, W. Jaegermann, G. Centi, J. Pérez-Ramírez, J.R. Galán-Mascarós, S. Perathoner, *Energy and Environmental Science* **2023**, *16*, 1644-1661.
2. C. Ampelli, F. Tavella, D. Giusi, A.M. Ronsisvalle, S. Perathoner, G. Centi, *Catalysis Today* **2023**, *421*, 114217.

Acknowledgements

This work was funded by the European Union through the H2020 Project "SUPERVAL" (ID: 101115456) and by the Italian Ministry for Universities and Research (MUR) through the FISA Project "SCOOP" (FISA-2022-00277) and NEST Spoke 9 Project "eCO_2", which are gratefully acknowledged.

Implementation of Catalytic Technologies for Mitigation of Humid, Lean Methane Exhaust Streams; Technological Hurdles for Industrial Implementation

Matthew DREWERY*[1], Matthew BLIGH[1], Ryan NOON[1], Luke HARVEY[1], Martin HARTMANN[2], Wilhelm SCHWIEGER[2], Eric M KENNEDY[1], Michael STOCKENHUBER[1]
[1]*University of Newcastle, Chemical Engineering, University Drive, Callaghan, Australia.*
[2]*Friedrich Alexander Universität, Chemical and Bioengineering, Egerlandstr, Erlangen, Germany.*
** Matthew.Drewery@newcastle.edu.au*

Significance and Relevance

The current study examines the development of catalytic technology and its potential to reduce anthropogenic, fugitive greenhouse emissions with a focus on the difficulties associated with implementing catalytic technologies in commercial applications. Specifically, an understanding of catalyst activity and mechanisms of deactivation is crucial for the development of a system which exhibits the stability necessary for industrial applications.

Preferred and 2nd choice for the topic: Air cleaning and combustion; Automotive and stationary emission control.
Preferred presentation: Oral only

Introduction and Motivations

An increased need to minimize fugitive greenhouse gas (GHG) emissions has put pressure on industries to reduce their associated emissions, in some instances deemed a necessary requirement to maintain financial viability. Recently, methane has gained attention due to its significantly higher global warming potential[1], leading to the development of systems to mitigate fugitive emissions, particularly those associated with mining and stationary power generation. For mining applications, very low concentrations of methane (<1%) are emitted in the ventilation exhaust, with very high flowrates (100 – 600 m^3/s) contributing to approximately 70% of the GHG emissions associated with the sector. For these applications, catalytic technologies offer several advantages over traditional thermal methods, with a demonstrated ability to oxidize lower concentrations of methane, operate at much lower temperatures and demand considerably lower energy input and physical footprint.

Materials and Methods

The catalytic oxidation of lean methane streams was examined in a stainless steel, tubular, fixed bed micro-reactor. Ventilation air methane (VAM) streams were simulated using flows of methane (0.2 – 0.7%) in humidified air. Catalysts were prepared via incipient wetness before being dried at 110°C for 20 hours. Sized catalysts (250 – 400 µm) were calcined *in situ* at 500°C prior to reaction.

Results and Discussion

The industrial implementation of catalytic technology for emission control requires the catalyst to exhibit high levels of activity and stability. Palladium catalysts have been identified as highly active oxidation catalysts, however there is no clear agreement on the major cause for loss of catalytic activity, with several potential processes discussed in the literature. The presence of water vapor in the feed stream is often not considered, however previous studies have reported that water competes with metal sites, transforming active palladium oxide to less active palladium hydroxide.

The current study examines oxidation of lean, humid methane streams over palladium on various support materials. Supports with differing properties were used to examine the effect of varying characteristics in minimizing catalyst deactivation and enhancing stability. The results displayed in Figure 1 show a significant difference in catalyst stability. Pd/Al_2O_3 was used to compare results with a standard, industrial oxidation catalyst, while MFI-structured supports were used to examine variations in chemical characteristics.

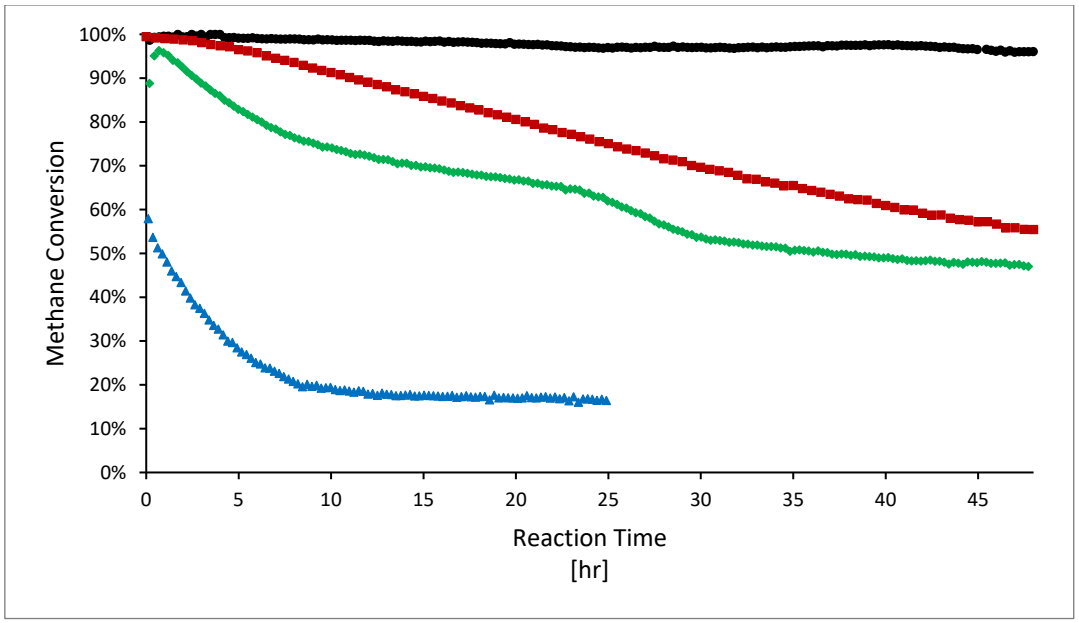


Figure 1: Catalyst stability under synthetic VAM conditions at 460°C and 100,00 h^{-1} GHSV. Feed composition 0.7% CH_4 in humidified air. Catalysts tested (1.2 wt% Pd); ●Pd/TS-1, ■Pd/Al_2O_3, ◆Pd/ZSM-5 (SiO_2:Al_2O_3 = 50), ▲Pd/ZSM-5 (SiO_2:Al_2O_3 = 23).

It is theorized that the differences in catalyst stability observed is a result of the varying presence of aluminum in the support framework, with increased Al content leading to a strong affinity for water vapor. It was observed that a decreased Al content results in a decreased concentration of Bronsted acid sites[2], which is proposed to inhibit hydroxyl accumulation on the catalyst surface[3]. It has been reported that this can also lead to an increased oxygen mobility, which can accelerate hydroxyl desorption, further impeding accumulation. This is further highlighted by the significant difference between the ZSM-5 catalysts, where increasing the SiO_2:Al_2O_3, thereby lowering associated Bronsted acid sites, greatly improved stability.

References

1. P. Da, et al., *Nat. Commun.* **2020**, *11(1)*, 4588.
2. D. P. Serrano, *Sep. Purif. Technol.*, **2007**, *54(1)*, 1.
3. A. Setiawan, et al., *Phys. Chem. Chem. Phys.*, **2016**, *18*, 10528.

Acknowledgements

The authors acknowledge the funding and support of Australian Coal Association Research Projects (ACARP) and the Australian Government Department of Industry, Science and Resources. The Australian Synchrotron (ANSTO), European Synchrotron Radiation Facility (ESRF) and Elettra have also provided support through the use of beamtime which developed insights on catalyst properties.

Impact of NO_2 on Sulfur Poisoning of Cu-SSZ-13 Catalysts

Afrina Zaman Shoronika[1], Poonam Rani[1], Rohil Daya[2], and William Epling[1]*
[1]*University of Virginia, Charlottesville, VA, USA*
[2]*Cummins Inc., Columbus, IN, USA*
*wse2t@virginia.edu

Significance and Relevance

Selective catalytic reduction of NO_X with NH_3 (NH_3-SCR) using Cu-CHA is commercially used to reduce NO_X emissions from diesel engine exhaust. Even with its commercial success, sulfur poisoning is a known degradation mechanism for Cu-CHA SCR catalysis. Here, we show how exposure to NO_2 affects sulfur species that form on Cu-SSZ-13, and that sulfation affects the formation of ammonium nitrate and copper nitrate during NO_2 exposure. The extent of NO_2 exposure changes the distribution of sulfur species on the catalyst surface, with long NO_2 exposure times leading to more challenging desulfation. The insights from this research can help design desulfation strategies.

Preferred and 2nd choice for the topic: Automotive and stationary emission control, fundamental advances in understanding catalysis
Preferred presentation: Oral only / Oral preferred

Introduction and Motivations

Selective catalytic reduction of NO_X with NH_3 (NH_3-SCR) using Cu-SSZ-13 is commercially used to reduce NO_X emissions from diesel engine exhaust. Among several reactions that occur over the SCR catalyst, the most discussed include the standard and fast SCR reactions, with the latter dependent on NO_2: $2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$. It is generally known that Cu-SSZ-13 is vulnerable to sulfur deactivation by SO_2, SO_3, and H_2SO_4 present in the exhaust. Though sulfur poisoning during standard SCR reaction conditions is relatively well-studied,[1] key questions remain about the impact of sulfur on the fast SCR process. Here, we studied how SO_2 affects the interaction between NO_2 and Cu-SSZ-13 and how NO_2 affects the interaction between SO_2 and Cu-SSZ-13.

Materials and Methods

A monolith-supported Cu-SSZ-13 catalyst with 600 cells per square inch (cpsi) was provided by Cummins Inc. The catalyst samples were formed to 2.9 cm in length, 45 cells and 0.89 g in weight. The total flow was 1400 sccm, corresponding to a gas space velocity of 60000 h^{-1}. Catalysts were pretreated with 10% O_2, 7% H_2O and balance N_2 for 4 h at 550 °C before use. SO_2 exposure included 30 ppm SO_2 for 21 h at 400 °C, followed by pretreatment with 10% O_2 and balance N_2 also at 400 °C. For the set of experiments described in this abstract, the sample was cooled to 200 °C and then exposed either to (i) NO_2, (ii) NH_3, then NO_2, or (iii) $NO+NH_3$, then NO_2, all typically followed by temperature programmed desorption (TPD) from 200 to 900 °C with a 10 °C/min heating rate. Other NO_2-focused experiments were run and the results of those will be presented also.

Results and Discussion

After SO_2 exposure, $ZCuSO_4$ forms from ZCuOH.[1] Our results show that exposing the sample to NO_2 after this sulfur exposure leads to less NO_2 reacted with Cu, and the TPD confirms that less nitrate was formed relative to a sample that had not been exposed to SO_2. Our results also demonstrate that when exposing the $ZCuSO_4$ to NH_3 or $NO+NH_3$, $(NH_4)_2SO_4$ forms, E1.

$$2NH_3 + ZCuSO_4 + 2H_2O \rightarrow (NH_4)_2SO_4 + ZCuOH \quad \text{E1}$$

When the sample is then exposed to NO_2, we show that the following reactions occur,[2]

$$2ZCuOH + 3NO_2 \rightarrow 2ZCuNO_3 + NO + H_2O \quad \text{E2}$$

$$2NO_2 + 2NH_3 \rightarrow NH_4NO_3 + N_2 + H_2O \quad \text{E3}$$

The $ZCuNO_3$ from E2 and $(NH_4)_2SO_4$ from E1 can react through a series of reactions summed up by E4

$$2ZCuNO_3 + 2(NH_4)_2SO_4 + 3NO_2 \rightarrow 2ZCuSO_4 + 4NH_4NO_3 + 0.5N_2 \quad \text{E4}$$

Finally, NH_4NO_3 decomposes to N_2O and H_2O according to the following equation

$$NH_4NO_3 \rightarrow N_2O + 2H_2O \qquad E5$$

Our results suggest that these reactions occur sequentially/simultaneously, and to show that, here we use an example where we varied NO_2 exposure times after a SO_2 then NO+NH_3 exposure, and then performed a TPD experiment. Figure 1A and B show that with 0.5 h and 1 h NO_2 exposure, the NO_2 concentration did not reach 300 ppm. For these NO_2 exposures, NO_2 was still reacting - we conclude that $(NH_4)_2SO_4$ was still present, so the nitrate formed via E2 was still reacting with $(NH_4)_2SO_4$ (E4), therefore the NO_2 is still being consumed in reforming a nitrate. With the 2 h NO_2 exposure, the inlet 300 ppm concentration was reached, Fig 1C, because 2 h was enough to consume all the $(NH_4)_2SO_4$ via E4, allowing the build up and saturation of Cu nitrates. Following this logic, with the shorter NO_2 exposure times, there should be no $ZCuNO_3$, since the NO_2/nitrate was reacting with the $(NH_4)_2SO_4$, but there should be $CuSO_4$ and NH_4NO_3 from E3 and E4, and the residual $(NH_4)_2SO_4$. First, the absence of NO_2 during the TPD (Fig 1D and E) supports the absence of $ZCuNO_3$. With the nitrates/NO_2 reacting with the $(NH_4)_2SO_4$, the $(NH_4)_2SO_4$ should decrease, and $CuSO_4$ should increase with NO_2 exposure time, which aligns with the TPD results in the bottom panel of Figure 1, where the low-temperature SO_2 peak originates from $(NH_4)_2SO_4$ and the higher-temperature release is from $CuSO_4$.[3] If with the 2 h NO_2 exposure, the $(NH_4)_2SO_4$ is consumed and the NH_4NO_3 has had time to decompose (E5), there should be no N_2O or low temperature SO_2 release in Fig 1F, which is indeed the case. Only $ZCuNO_3$ and $CuSO_4$ should be present, which is why we see NO_2 and the high temperature SO_2 peaks. These results all show that initially $ZCuNO_3$ forms from ZCuOH and reacts with $(NH_4)_2SO_4$. Once $(NH_4)_2SO_4$ is depleted, only $ZCuNO_3$ persists which ultimately decomposes during TPD.

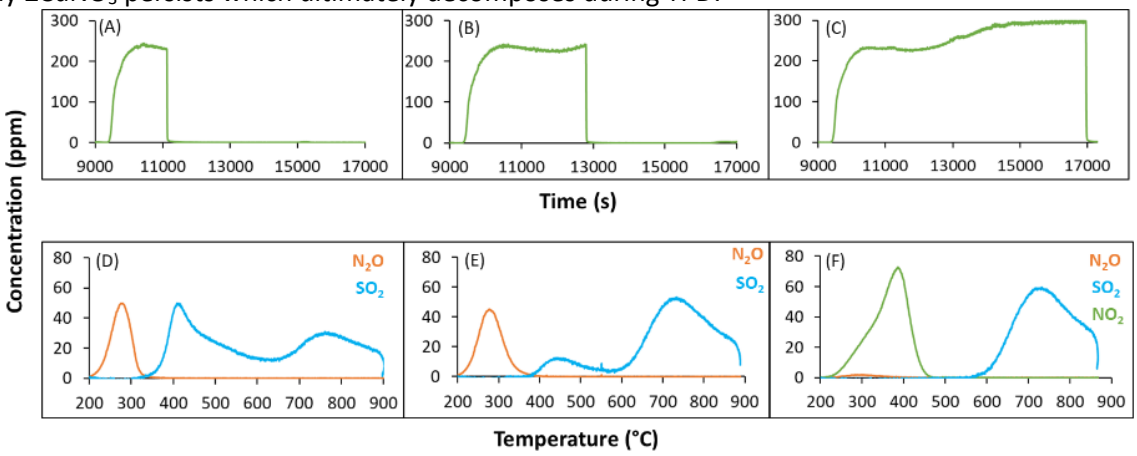


Figure 1. Top panel - NO_2 profiles, and bottom panel - corresponding TPD profiles after SO_2, then NO+NH_3 followed by NO_2 exposures, for different NO_2 exposure periods on Cu-SSZ-13 at 200 °C.

Our study shows that Cu and ammonium nitrate formation are impacted by SO_2 exposure, and Cu and ammonium sulfate formation are impacted by NO_2 exposure. This has implications for desulfation strategies and SCR design.

References

1. K. Mandal, P. Rani, Y.-R. Chen, A. Wijerathne, K. Nam, K. Meena, D.A. Kiani, R. Daya, W.S. Epling, C. Paolucci, *Applied Catalysis B: Environment and Energy* **2024**, *358*, 124361.
2. C. Liu, G. Malta, H. Kubota, T. Toyao, Z. Maeno, K.J. Shimizu, *Journal of Physical Chemistry C* **2021**, *125*, 21975–21987.
3. A. Wang, L. Olsson, *Chemical Engineering Journal* **2020**, *395*, 125048

Acknowledgements

The authors acknowledge the financial support provided by Cummins Inc.

Synergistic effect between manganese and copper oxides in boosting low-temperature catalytic oxidation of indoor pollutants

Nadia GRIFASI, Giorgio DEMICHELIS, Samir BENSAID, Nunzio RUSSO, Debora FINO, Marco PIUMETTI*
Polytechnic of Turin, Department of Applied Science and Technology, Corso Duca Degli Abruzzi, 24, 10129, Turin, Italy
* marco.piumetti@polito.it

Significance and Relevance

This study presents insights into the field of environmental catalysis by demonstrating the successful oxidation of pollutants at low temperatures, a challenging task in catalytic processes. The significant impact of this work concerns the achievement of promising results without using precious metals, which typically drive high-performance catalysts. The synergy between copper and manganese positively influenced the catalytic performance, enhancing the overall activity, and allowing it to completely oxidize pollutants at low temperatures. Moreover, the use of a simple and reproducible synthesis redox technique further amplifies the potential for scaling this approach, offering a cost-effective solution for addressing environmental pollution.

Preferred and 2nd choice for the topic: Air cleaning and combustion/Automotive and stationary emission control
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

In recent years, there has been growing interest in air purification, particularly with regard to indoor air pollution, which can pose greater risks to health than outdoor pollution. Among the various pollutants present in the atmosphere, Volatile Organic Compounds (VOCs), commonly found in products like paints and cleaning agents, are among the most prevalent[1]. One promising method for eliminating these contaminants is catalytic oxidation at low temperatures. Manganese oxide catalysts show great potential in this area, but the temperatures required to effectively remove common indoor pollutants like CO and ethylene remain relatively high[2]. However, mixed oxides such as copper-manganese oxides have demonstrated significant catalytic activity for the oxidation of CO and VOCs, offering advantages in terms of effectiveness, longevity, and cost-efficiency[3]. The synergistic effect between copper and manganese oxides could further enhance their catalytic performance, enabling pollutant removal at lower temperatures. This approach shows considerable promise for improving indoor air quality and promoting the health and well-being of individuals in enclosed spaces.

Materials and Methods

Manganese oxides with different copper loading (1-10 wt.% of Cu) were synthesized through Solution Combustion Synthesis (SCS) introducing 1 wt.% and 3wt.% of copper in the structure. To avoid phase segregation as the amount of copper in the structure increases, a different synthesis (redox) technique has been proposed in the case of 10wt.%, introducing some modifications to the procedures found in the literature. The synthesized materials were subsequently characterized through different physicochemical techniques and then the catalytic activity was investigated by simulating a real polluted atmosphere containing CO or ethylene as target molecules in a concentration of 100 ppm over 50 mg of catalyst. Finally, time-on-stream (TOS) analyses were carried out on the best-performing catalyst to investigate the performance and stability of this sample better.

Results and Discussion

The presence of copper within the structure demonstrated an extremely positive impact on catalytic performance, as revealed in Figure 1. A preliminary screening was carried out by testing CO as a target molecule. In this context, when comparing the samples obtained via the SCS method, a small increase in copper content (from 1wt.% in $Cu_{0.01}Mn_{0.99}$_SCS to 3wt.% in $Cu_{0.03}Mn_{0.97}$_SCS) significantly improved the catalytic activity, enabling complete oxidation of CO at a relatively low temperature of 100 °C in the case of $Cu_{0.03}Mn_{0.97}$_SCS sample. These preliminary results were then compared to those obtained with $Cu_{0.1}Mn_{0.9}$_redox, which showed surprising results. Specifically, the CO was fully oxidized at an

incredibly low temperature of just 23 °C, maintaining a 100 % conversion for a continuous 6-hour period in the presence of the reagent mixture. This outstanding catalytic performance could be attributed to the increased surface area (329 m^2g^{-1} against 15 m^2g^{-1} and 7 m^2g^{-1} for $Cu_{0.01}Mn_{0.99}$_SCS and $Cu_{0.03}Mn_{0.97}$_SCS) and the enhanced Mn-Cu interfaces, which create defects that further boost catalytic activity. Subsequently, since both $Cu_{0.03}Mn_{0.97}$_SCS and $Cu_{0.1}Mn_{0.9}$_redox demonstrated the best performances, they were also tested for the oxidation of ethylene, which is much more complex to oxidize at low temperatures. Once again, the redox sample exhibited superior results, achieving over 95 % conversion at 150 °C. These results demonstrate the effectiveness of this catalyst in oxidizing complex molecules without the use of noble metals, utilizing a simple and scalable synthesis procedure.

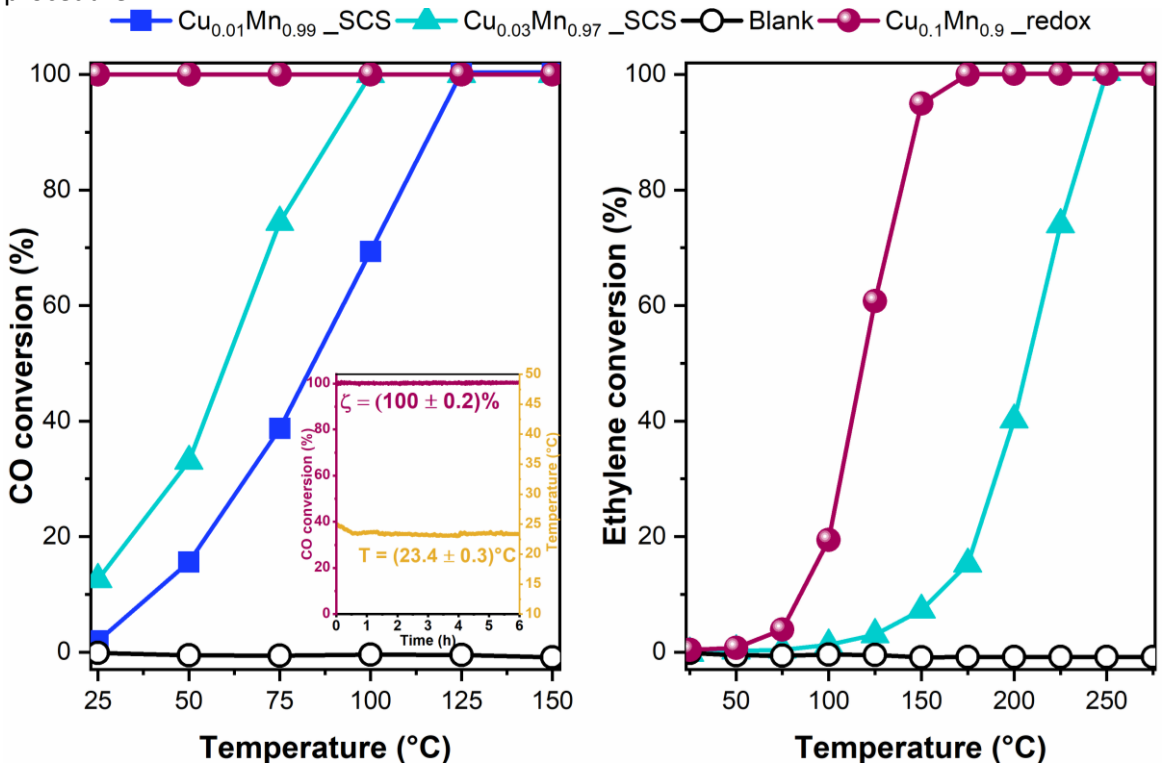


Figure 1 Catalytic oxidation of CO (left) and ethylene (right) over the investigated samples.

In conclusion, the topic proposed in this work is particularly challenging due to some limitations (i.e., low concentrations of pollutants, low temperatures adopted, and the complexity of the target molecules). However, the promising results achieved without the use of noble metals are a positive indication for the development of more cost-effective technologies. Further investigations into the reaction mechanism and deeper characterizations are currently ongoing to better understand the synergistic interactions between the Mn and Cu phases, along with the amounts of reactive oxygen species and structural defects. New pollutants will also be tested and optimizations will be pursued to reduce the temperature required for VOC oxidation, thus enhancing catalytic performance.

References

1. Guo, Y., Wen, M., Li, G., An, T. Appl Catal B, **2021**, 281.
2. Grifasi, N., Sartoretti, E., Montesi, D., Bensaid, S., Russo, N., Deorsola, F. A., Fino, D., Novara, C., Giorgis, F., Piumetti, M. Appl Catal B, **2025**, 362.
3. Cocuzza, C., Sartoretti, E., Novara, C., Giorgis, F., Bensaid, S., Russo, N., Fino, D., Piumetti, M. Catalysis Today, **2023**, 423.

Acknowledgements

This study was carried out within the Guardian project – funded by European Union – Next Generation EU within the PRIN 2022 PNRR program (D.D. 1409 del 14/09/2022 Ministero dell'Università e della Ricerca). This manuscript reflects only the authors' views and opinions and the Ministry cannot be considered responsible for them.

Kinetics of site transformations in Pd/AEI zeolite for NO_x adsorption

Petr KOČÍ[*,1], Tetyana ZHELEZNYAK[1], Richard KNOPP[1],
Maria Pia RUGGERI[2], Djamela BOUNECHADA[2], Andrew P.E. YORK[2]
[1]*University of Chemistry and Technology, Dept. of Chemical Engineering, Technická 5, Prague, Czech Republic.*
[2]*Johnson Matthey Technology Centre, Blounts Court Road, Sonning Common, Reading, UK.*
**petr.koci@vscht.cz*

Significance and Relevance

Pd ion exchanged into BEA, ZSM-5, SSZ-13 or AEI zeolite are contenders in passive NOx adsorber (PNA) technologies for diesel exhaust gas aftertreatment under cold start conditions[1,2]. However, water and CO-induced Pd agglomeration into clusters and nanoparticles decreases the number of active Pd sites available for NO adsorption. The combination of lab experiments and kinetic modelling allows us to build a physically relevant, predictive model of PNA activity and adsorption capacity depending on the trajectory of operating conditions (temperature, water content, CO and NO concentration), and to explore possible catalyst reactivation strategies for improved performance of the catalyst under real world conditions.

Preferred and 2nd choice for the topic: Automotive and stationary emission control, Air cleaning and combustion
Preferred presentation: Oral preferred

Introduction and Motivations

In passive NO_x adsorber (PNA), NO is adsorbed at low temperature and released once the exhaust temperature is warm enough for downstream SCR catalysts to be active. Pd interconverts between single atoms and clusters within zeolites depending on the operating conditions. Pd has been described as water-solvated and detached from the zeolite at low temperature, while under dry conditions or at higher temperatures, the Pd is associated with the zeolite[3]. Furthermore, reduction of Pd ions into the metallic state promotes their agglomeration, hence the effect of reducing agents such as CO on Pd clusters formation and growth of larger Pd nanoparticles outside the zeolite framework must be considered. Pd agglomeration decreases the number of active Pd sites available for NO adsorption, and strategies for slowing down or even reversing this process must be developed. When oxidized, small Pd particles can either disintegrate and reform the ion-exchanged species or agglomerate and form larger particles that reside on the external of the zeolite[4].
Kinetic modeling allows calculation of reaction rates under a variety of exhaust gas conditions so that conversion and overall emissions reduction performance can be computationally predicted. Standard kinetic models, however, use fixed values of kinetic parameters for the given catalyst. Expanding the models to include how the catalyst active sites evolve is critical. This means including rate laws for changes in active site concentrations as a function of reaction environment conditions.

Materials and Methods

A model 1% Pd/AEI catalyst was prepared by incipient wetness impregnation of Pd nitrate into AEI zeolite with Si-to-Al ratio 20, followed by 2 h of calcination at 500 °C and 16 h of high-temperature treatment at 750 °C in air, resulting in Pd ions exchanged inside the zeolite structure. STEM images showed no Pd nanoparticles present in the prepared catalyst. H_2 temperature programmed reduction has been used to characterize the amounts of ion-exchanged and PdO particles, and NO adsorption with temperature-programmed desorption were used to quantify the number of active Pd sites in the zeolite framework.
Each PNA experiment was performed with 0.4g of the catalyst powder in a tubular lab reactor. The feed always contained 5% O_2, 5% or 10% H_2O and 10% CO_2 and the total flow rate was 2 dm^3/min. The test included isothermal NO adsorption at 100°C, desorption temperature ramp to 500°C, cooling

down, 5 or 20 min deactivation period at various temperatures, CO, NO and H_2O levels, and repeated NO adsorption and temperature programmed desorption. Finally, the possibility of catalyst reactivation by Pd redispersion in the zeolite structure was tested under oxidizing conditions at 500 °C and 750°C.

Results and Discussion

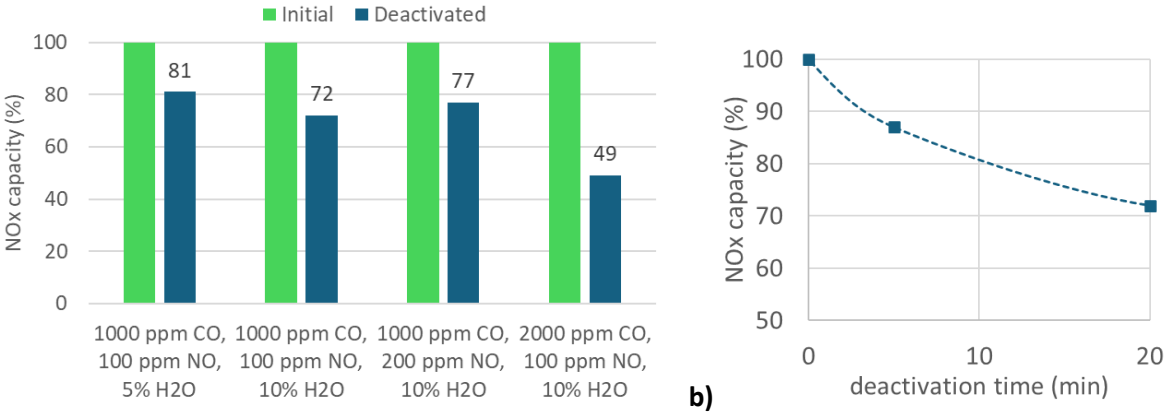


Figure 1. Change in NO adsorption capacity due to Pd agglomeration during 20 min in Pd/AEI zeolite at 100 °C. a) Impact of CO, H_2O and NO. b) Impact of deactivation time.

Pd agglomeration at low temperatures is accelerated by water and CO, Figure 1. The corresponding mechanism involves formation of Pd hydrates and carbonyls that allow detachment of Pd from the zeolite framework and make it mobile. The impact of CO on the process is crucial as it can reduce Pd ions into metallic state and promote the formation of Pd clusters and nanoparticles. In contrast, increased NO concentration slows down the deactivation as it competes with CO for the adsorption on Pd sites, which weakens CO impact. The deactivation rate is practically constant at temperatures 80-120 °C and effectively decreases at higher temperatures, which is caused by (i) the decreasing extent of Pd hydration that makes Pd less mobile and supports its anchoring into the zeolite framework, and (ii) the increasing CO oxidation rate that effectively consumes all CO near the inlet.

Based on the experimental data, kinetic equations for Pd sites transformation are expressed as functions of actual site concentration, gas composition and corresponding coverage on active sites, metal oxidation state and temperature. Pd cluster and nanoparticle formation and growth are affected by Pd reduction steps. The lab experiments provide data for evaluation of rate coefficients for individual site transformation steps as well as their possible reversibility under different operating conditions. While complete Pd redispersion into zeolite framework requires 750°C, partial catalyst regeneration can be achieved below 500°C.

Acknowledgements
This work was financially supported by the Czech Science Foundation (GA 23-07137L).

References

1. H.-Y. Chen, J.E. Collier, D. Liu, L. Mantarosie, D. Duran-Martin, V. Novák, R.R. Rajaram, D. Thompsett, *Catal. Letters.* 146 (2016) 1706–1711.
2. A. Kvasničková, P. Kočí, Y. Ji, M. Crocker, *Catal. Letters*. 150 (2020) 3223–3233.
3. K. Mandal, Y. Gu, K.S. Westendorff, S. Li, J.A. Pihl, L.C. Grabow, W.S. Epling, C. Paolucci, *ACS Catal.* 10 (2020) 12801–12818.
4. S. Yasumura, H. Ide, T. Ueda, Y. Jing, C. Liu, K. Kon, T. Toyao, Z. Maeno, K. Shimizu, *JACS Au.* 1 (2021) 201–211.

A novel gas-phase approach to control selectivity in ethanol photo-oxidation on metal-doped TiO_2/Ti gauze photoanodes

Francesco TAVELLA[*,1], Luana DE PASQUALE [1], Siglinda PERATHONER[1], Gabriele CENTI[1], Chiara GENOVESE[1], Claudio AMPELLI[1]

[1] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences (ChiBioFarAm) – University of Messina, ERIC aisbl and CASPE/INSTM, V.le F.Stagno d'Alcontres, 31 – 98166 Messina, Italy.*

** francesco.tavella@unime.it*

Significance and Relevance

Artificial leaf-type systems are small-scale electrochemical devices designed for the distributed production of chemical and fuels using renewable energy sources, e.g. solar power.[1] The cathodic reaction is the electrocatalytic reduction of abundant small molecules, like carbon dioxide (CO_2) and dinitrogen (N_2), while the counter half-reaction is typically the Oxygen Evolution Reaction (OER), which takes place at the anodic part. However, the OER is quite challenging due to its large overpotential, being the rate-limiting step in water-splitting electrolysers. Additionally, although water oxidation generates protons needed for the cathodic reduction reactions, the evolved oxygen (O_2) is unsuitable for distributed industrial applications due to the lack of efficient end-users for dilute oxygen streams. In this work, we explored alternative anodic reactions for artificial leaf devices and water electrolysers to address these limitations, aiming to reduce overpotential and lower power requirements for driving the electrocatalytic reduction. We introduced (bio)ethanol into the anode, where it was oxidized to acetaldehyde and acetic acid. The influence of different metals (Ag or Pd) used to decorate TiO_2/Ti gauze-based photo-anodes was investigated, and unconventional gas phase conditions were compared with the common use of a liquid electrolyte. Results showed a shifted selectivity to acetic acid in gas-phase operation, while only acetaldehyde was observed in conventional liquid phase configuration.

Preferred and 2nd choice for the topic: Photocatalysis and photo-electrocatalytic approaches, solar energy utilization – Green chemistry and biomass transformation, renewable resources conversion
Preferred presentation: Oral preferred or Short Oral / Poster

Introduction and Motivations

Artificial photosynthesis to directly convert CO_2 (and/or N_2) and water into valuable industrial chemicals is one of today's major challenges to address growing energy demands and mitigate climate change. This reaction can be performed in advanced photo electro-chemical (PEC) devices,[2] where a photoactive anode is irradiated by sunlight to generate protons for the reduction reaction. Typically, the protons migrate through an ion-exchange membrane to the cathode side, while O_2 evolves from the anodic compartment. In general, the limited production rates and profit margins of PEC devices explored so far have hindered strong interest from the industry. In this work, we present a novel PEC compact flow device designed to minimize energy losses caused by overpotential. We focused on the development and behaviour of the photoanode, which can operate both in presence of a liquid electrolyte or under unconventional gas-phase (electrolyte-less) conditions. The photo-anode consists of highly ordered TiO_2 nanotube arrays grown on Ti gauze (then decorated with metal nanoparticles), specifically designed to improve light harvesting and enhance mass and charge transfer processes. We studied the role of the gas-phase configuration in addressing selectivity of (bio)ethanol oxidation to acetaldehyde and/or acetic acid, considering the effect of different deposited metals.

Materials and Methods

TiO_2 nanotubes were synthesized on Ti gauze via controlled anodic oxidation.[3] Prior to anodization, the metallic supports were cleaned by sonication in isopropanol for 30 min, followed by drying in air at 100 °C. The clean substrate was then placed in a two-electrode electrochemical cell, using an electrolyte containing 2 wt% H_2O and 0.33 wt% NH_4F in ethylene glycol, under a constant voltage of 50

V for 60 min. After anodization, the samples were annealed at 450 °C for 3 h to induce the crystalline anatase phase. Silver (Ag) or palladium (Pd) nanoparticles were then deposited onto the TiO_2/Ti gauze surface using the photo-deposition technique. The PEC cell, made of Plexiglas, consists of two separate chambers for cathodic and anodic reactions, as shown in Figure 1a. In the liquid-phase configuration, the device is connected to two storage tanks for electrolyte circulation. In the gas-phase configuration, an external hot plate pre-heats a 20 vol% ethanol solution, while an inert gas flow moves the vapours directly into the anode chamber.

Results and Discussion

Figure 1b shows a picture and two SEM images of Ti/TiO_2 electrode. Vertically aligned TiO_2 nanotubes with a circular shape were formed on the round surface of the Ti gauze, exhibiting an opening diameter of around 52 nm. The final electrode shows two types of porosity: a mesoporosity due to the TiO_2 nanotubes, and a macroporosity due to the mesh structure of the Ti gauze. Photo-electrocatalytic tests were conducted by irradiating the photoanode with a solar simulator (300 W, Xe arc lamp, 1 sun). The photoanode (i.e. metal-doped TiO_2/Ti gauze) was coupled with a Nafion membrane to form a MEA (Membrane Electrode Assembly), effectively reducing overpotential. In gas-phase configuration, no liquid electrolyte was introduced into the cathode compartment. Results showed acetaldehyde as the only oxidation product observed under conventional liquid-phase configuration. Contrarily, in gas-phase configuration, the selectivity shifted partially to acetic acid formation, with Faradaic efficiency of 1.6% and 3.6% for Pd and Ag-doped TiO_2-Ti gauze, respectively, highlighting the advantages of operating without a liquid electrolyte to boost the oxidation process.

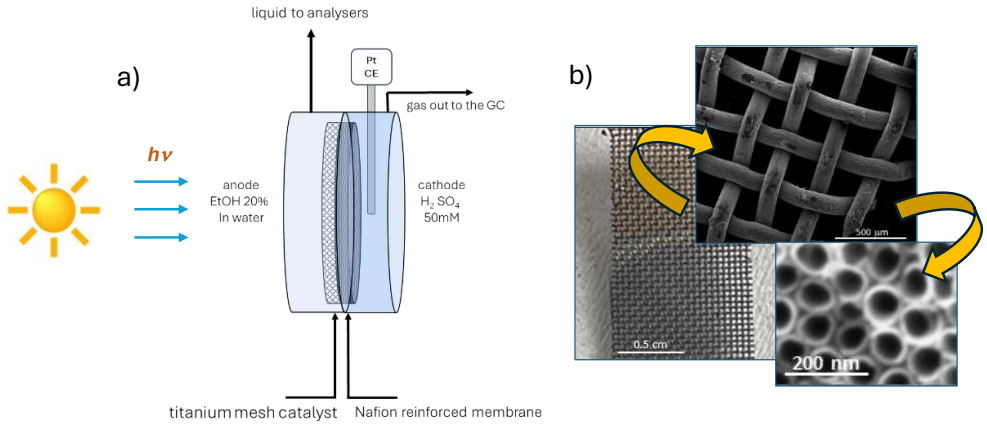


Figure 1: a) Schematic representation of the compact photo-electrocatalytic device working under unconventional gas-phase conditions; b) pictures and SEM images of the Ti/TiO_2 gauze electrode.

References

1. C. Ampelli, D. Giusi, M. Miceli, T. Merdzhanova, V. Smirnov, U. Chime, O. Astakhov, A.J. Martín, F.L.P. Veenstra, F.A. Garcés-Pineda, J. González-Cobos, M. García-Tecedor, S. Giménez, W. Jaegermann, G. Centi, J. Pérez-Ramírez, J.R. Galán-Mascarós, S. Perathoner, *Energy Environ. Sci.* **2023**, *16*, 1644-1661.
2. C. Ampelli, F. Tavella, D. Giusi, A.M. Ronsisvalle, S. Perathoner, G. Centi, *Catal. Today* **2023**, *421*, 114217;
3. L. De Pasquale, F. Tavella, V. Longo, M. Favaro, S. Perathoner, G. Centi, C. Ampelli, C. Genovese, *Molecules* **2023**, *28*, 3378

Acknowledgements

This work was funded by the European Union through the H2020 Project “SUPERVAL” (ID: 101115456) and by the Italian Ministry for Universities and Research (MUR) through the FISA Project “SCOOP” (FISA-2022-00277) and NEST Spoke 9 Project “eCO_2”, which are gratefully acknowledged.

Two In, One Out: Molecular Architectures for Efficient Photon Upconversion

Soumitra MANNA[1], Francesca S. FREYRIA[2], Barbara BONELLI[2], Jenny G. VITILLO[*,1]
[1] *Department of Science and High Technology and INSTM, Università degli Studi dell'Insubria, Via Valleggio 9, I-22100 Como, Italy.*
[2] *Department of Applied Science and Technology and INSTM-Unit of Torino Politecnico, Corso Duca degli Abruzzi 24, Politecnico di Torino,10129 Torino, Italy.*
** jenny.vitillo@uninsubria.it*

Significance and Relevance

Triplet-triplet Annihilation Up Conversion (TTA-UC) converts two photons into one having almost double the energy, allowing the exploitation of visible or NIR photons in devices having larger band gaps. Unlike other UCs, it works also with non-coherent and relatively low-intensity incident light, so being particularly promising for solar applications. Several molecules have been reported as TTA annihilators, but comprehensive analysis of their geometry is scarce in the literature. While most of the annihilators are known to be planar, some well-known emitters show twisted geometries. Because of the difficulties in simulating these systems in their working conditions, an empirical analysis of the criteria of a good annihilator can be very useful for the research field. Here we use Kohn-Sham Density Functional methods with the aim to find common geometrical and electronic properties among the different TTA families reported so far in the literature.

Preferred and 2nd choice for the topic: 1) Photocatalysis and photoelectrocatalytic approaches, solar energy utilization; 2) Sustainable and clean energy production and transport.
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

TTA-UC is a powerful process, because it allows to get what is perceived to be impossible in a normal absorption process, that is to have absorption although the frequency of the incident photons is lower than the band gap. This is possible because of the presence of molecules, the TTA-UC annihilators, that after excitation can form dimers involved in an entangled triplet state. Each dimer can decay with one of the monomers in the ground state ($_0$) while the other being in a singlet excited state ($_1$). This latter molecule can then relax by emitting a photon through the $_1 \rightarrow \ _0$ fluorescence that has twice the energy of the $_0 \rightarrow \ _1$ transition.[1]

The simulation of the dimer in the entangled triplet state is not easily achievable through time dependent density functional methods (TD-DFT) while its simulation using advanced multireference wave function-based methods is limited by the dimension of the dimeric systems and the corresponding active spaces, besides presenting significant difficulties in identifying the correct electronic configuration associated with it. [1]

In this work,[2] we have considered a novel approach to determine the characteristics of good TTA emitters. We have collected the different families of TTA-UC emitters reported so far in the literature and modeled them using DFT to find the common points that are shared among the molecules that are good TTA-UC annihilators.

Methods

All DFT calculations were performed using the *Gaussian 16* program. Geometry optimization was carried out by means of the Berny optimization algorithm with analytical gradient and default convergence thresholds. Unscaled, harmonic vibrational frequencies were computed analytically.

Results and Discussion

A collection of > 50 molecules reported as TTA-UC annihilators has been obtained through extensive review of the literature. Each of these molecules has been optimized by means of DFT and it has been verified to be a minimum of potential energy. The UV-Vis absorption spectrum has also been simulated using TD-DFT.

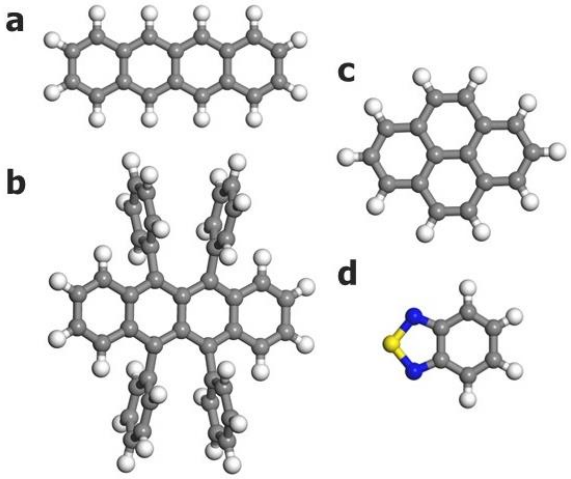


Figure 1 Structures of the most common TTA-UC annihilators in the literature: (a) tetracene, (b) rubrene, (c) pyrene, and (d) benzothiazole. Structures as optimized at the B3LYP/def2-TZVP level in their ground state. Color code: grey (carbon), yellow (sulfur), blue (nitrogen), white (hydrogen).

The key finding of this work is that most of the reported TTA-UC annihilators exhibit a planar structure in regions where the primary changes in electron density occur during $S_0 \rightarrow T_1$ and $S_0 \rightarrow S_1$ electronic transitions. This implies that the functional groups linked to these emitting cores should be carefully chosen to prevent structural distortions that can limit quantum yields. We also verified that geometrical distortions decrease the oscillator strengths for the $S_0 \rightarrow T_1$ and the $S_0 \rightarrow S_1$ transitions due to reduced aromaticity, as shown in electronic density maps. The condition of planarity for the observed TTA emitters applies to molecules undergoing TTA through the favourable S_1 pathway. However, few emitters exist with distorted core undergoing TTA through the less favourable T_2 pathway. The distortions in the molecular core occur to accommodate the bulky substituents to the core. Electron density maps of these molecules suggest that the distortion in molecular geometry facilitates the T_2-S_1 intersystem crossing leading to conversion of T_2 excitons to up-converted S_1 photons. Overall, the functional groups attached to the molecular core of annihilators play significant role in deciding the molecular geometry which in turn is associated with the observed TTA efficiency. These results linking a structural property with TTA-UC quantum yield represent an advancement in the field and they provide easy directions for more efficient design of new TTA-UC annihilators.[2]

References

1. X. Wang et al., *J. Mater. Chem. C*, **2020**, *8*, 10816.
2. S. Manna, J.G. Vitillo, in preparation.

Acknowledgements

This study was carried out within the « GREEN UP: GREENER NANOMATERIALS FOR UPCONVERSION IN PHOTOCATALYTIC APPLICATIONS» project –funded by the Ministero dell'Università e della Ricerca –within the PRIN 2022 program (D.D.104 -02/02/2022) funded by the European Union - Next Generation EU.
This manuscript reflects only the authors' views and opinions and the Ministry cannot be considered responsible for them.

Catalytical degradation of haloacetic acids (HAA) in H_2/CO_2/Xe-UV system – Advanced Reduction Process (ARP) for wastewater treatment

Łukasz Cichocki*, Grzegorz Boczkaj
Gdańsk University of Technology, Department of Sanitary Engineering,
St. Narutowicza 11/12, 80-233 Gdańsk, Poland.
**lukasz.cichocki@pg.edu.pl*

Significance and Relevance

Advanced reduction processes (ARPs) define a novel approach for water treatment using non-toxic reagents and catalysts to degrade harmful pollutants present in treated stream. Water pollution by haloacetic acids (HAAs) is a major environmental problem for which ARPs provide a novel solution. The possibility of treating water with carbon dioxide, commonly present in the atmosphere, makes ARPs doubly beneficial for the environment and people.

Preferred and 2nd choice for the topic: Degradation of persistent pesticides in CO_2 /HCOOH/Xe-UV – Advanced Raduction Process (ARP) for wastewater treatment

Preferred presentation: (Oral only **/** Oral preferred or Short Oral / Poster): Oral or Poster.

Introduction and Motivations

Advanced reduction processes (ARPs) represent an emerging approach to wastewater treatment, serving as an alternative to the extensively studied advanced oxidation processes (AOPs) [1-3]. The application of ARPs in water treatment, particularly through the use of catalysts and hydrogen while utilizing carbon dioxide, offers a modern and potentially effective method for degradation of water contamination. This approach is especially relevant for the degradation of haloacetic acids, which are primarily generated as byproducts of water disinfection involving chlorine-based compounds, as well as from industrial activities [4, 5].

Results and Discussion

Trichloroacetic acid was selected as the representative chemical compound for HAA, which is the most common pollutant from HAA group in water. The carbon dioxide-based process achieved >99% TCAA degradation and >90% dechlorination in 20 minutes. Degradation study and chloride concentration were studied by ion chromatography. The presented process is an excellent method to purify water from HAA using carbon dioxide. Further research in the paper was extended to investigate catalysts (metal-based on activated carbon) to further improve and reduce the time of treatment.

References

1. Askarniya, Z., et al., *Degradation of dicamba–a persistent herbicide-by combined application of formic acid and UV as an advanced reduction process.* Journal of Hazardous Materials, 2025: p. 137984.
2. Cichocki, Ł., et al., *First highly effective non-catalytic nitrobenzene reduction in UV/dithionite system with aniline production–Advanced reduction process (ARP) approach.* Chemical Engineering Journal, 2024. **479**: p. 147878.
3. Asadi, A.M.S., et al., *Catalysts for advanced oxidation processes: Deep eutectic solvents-assisted synthesis–A review.* Water Resources and Industry, 2024. **31**: p. 100251.
4. Chu, W., et al., *The formation of haloacetamides and other disinfection by-products from non-nitrogenous low-molecular weight organic acids during chloramination.* Chemical Engineering Journal, 2016. **285**: p. 164-171.

5. Wang, L., et al., *Photolysis and photocatalysis of haloacetic acids in water: A review of kinetics, influencing factors, products, pathways, and mechanisms.* Journal of hazardous materials, 2020. **391**: p. 122143.

Acknowledgements

The authors gratefully acknowledge financial support from the National Science Centre, Warsaw, Poland for project OPUS nr UMO-2021/41/B/ST8/01575.

Transient and catalytic NO direct decomposition by irradiating microwave

Maya CHATTERJEE, Misaki KIMURA, Masateru NISHIOKA, Masaru OGURA*
Institute of Industrial Science, The University of Tokyo, Komaba, Tokyo, Japan.
** oguram@iis.u-tokyo.ac.jp*

Significance and Relevance

Nitrogen oxides could be removed by a two-step catalytic process using pulsatile microwave irradiation onto the adsorbents of nitrogen oxides such as Pd/zeolites and Pt-Ba/Al_2O_3, followed by an active catalyst for direct decomposition of nitric oxides such as Cu/zeolites.
Preferred choice for the topic: Automotive and stationary emission control
Preferred presentation: Oral preferred

Introduction and Motivations

Purification of nitrogen oxides NOx from combustion exhausts is still highly required in terms of higher efficiency in the combustion process at higher temperatures to decrease carbon dioxide CO_2 emission. Ammonia NH_3 or urea is now utilized as the selective reductant of NOx toward not only heavy-duty mobile sources, but also to ships, power stations, and so on to generate energy for our lives. The NH_3-utilized selective catalytic reduction using Cu/zeolites and vanadia-type oxides are well known catalytic technologies, but the system to dose NH_3 or urea to the exhaust, as well as catalytic process for eliminating residual NH_3 in the exhaust is quite complicated to load on the mobile sources. Although oxidizing atmosphere in combustion exhaust is preferable to catalyze oxidation, CO_2 is inevitably formed during the NOx reduction when hydrocarbons and/or carbon monoxide are used as the reductant. We are highly requested to find a simple and good catalyst/catalytic system for NOx removal without any CO_2 emission. Therefore, we revisited to investigate NO direct decomposition. To realize minimum energy catalytic process, pulsatile microwave irradiation is adopted onto adsorbed NO at lower temperatures on typical NOx adsorbents such as Pd/zeolites and Pt-Ba/Al_2O_3. The lower temperatures mean where the catalysis is never expected, therefore we use adsorption and concentration of NOx prior to activate NO decomposition activity on Cu/zeolites by microwave[1].

Results and Discussion

Figure 1 shows the amounts of adsorbed NOx in excess O_2 at 473 K (left bar), and desorbed NOx colored by temperatures for the desorption (right bar), on each typical NOx adsorber[2]. The difference between the amounts could be explained by catalysis on Cu/ZSM-5 for NO direct decomposition occurred at high temperatures over 773 K, and by strong adsorption of NOx on Pt-Ba/Al_2O_3 even at 773 K. Pd/zeolites are known as a PNA material at lower temperatures, so that the amounts of NO adsorbed on and desorbed from the Pd/Beta were well balanced, and never showed NO decomposition activity. Pt is quite important to store NOx on Ba species, so that Ba/Al_2O_3 did not show its efficiency for NOx storage. Therefore, the combination of NOx adsorber even in O_2-rich atmosphere and NO decomposition catalyst will induce higher efficiency for NO removal without using any reductant in the stream, which will be presented in the conference.

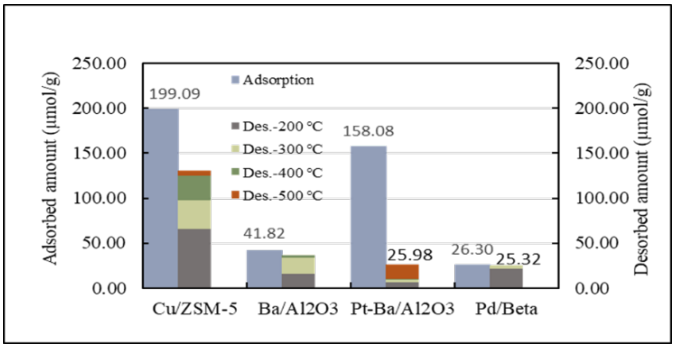


Figure 1 NOx adsorption/desorption properties on NOx adsorbers.

References

1. S. Harada, T. Ohnishi, M. Ogura, *Chem. Lett.* **2016**, *45*, 1283. K. Kawakami, M. Ogura, *Catal. Today* **2015**, *242B*, 343.
2. M. Chatterjee, M. Ogura, in preparation.

Removal of formaldehyde, carbon monoxide and methane from lean gas engine exhaust gases using precious metal-free catalysts

Kalle WEIDAUER[1], Sven KURETI[1]
[1]*TU Bergakademie Freiberg, Institute of Energy Process Engineering and Chemical Engineering, Fuchsmühlenweg 9D, 09599 Freiberg, Germany.*
Kalle.Weidauer@iec.tu-freiberg.de, **Sven.Kureti@iec.tu-freiberg.de*

Significance and Relevance

Manganese and iron containing perovskite-type catalysts show high HCHO, CO and CH_4 oxidation activity in lean exhaust gases of stationary gas engines. Furthermore, the CH_4 oxidation performance was investigated at elevated pressures towards a potential pre-turbo application.

Preferred and 2nd choice for the topic: Automotive and stationary emission control / -
Preferred presentation: Oral only

Introduction and Motivations

The exhaust gas aftertreatment of lean-burn gas engines for stationary and mobile applications is of great importance for the CO_2-neutral generation of electricity and heat as well as for the mobility of the future. The engines are particularly sustainable when biogenic fuels such as biomethane are used. However, unburnt methane (CH_4) contributes to the greenhouse effect (by a factor of 25 compared to CO_2), while toxic carbon monoxide (CO) and formaldehyde (HCHO) are also emitted[1-3].

The most important catalysts for the oxidation of these pollutant are based on precious metals such as platinum and palladium, which are rare and cost-intensive. However, the catalysts are not stable with regard to the CH_4 oxidation[4]. Therefore, this paper addresses the development of novel catalysts for the removal of CH_4 as well as CO and HCHO using Fe and Mn containing perovskites.

Results and Discussion

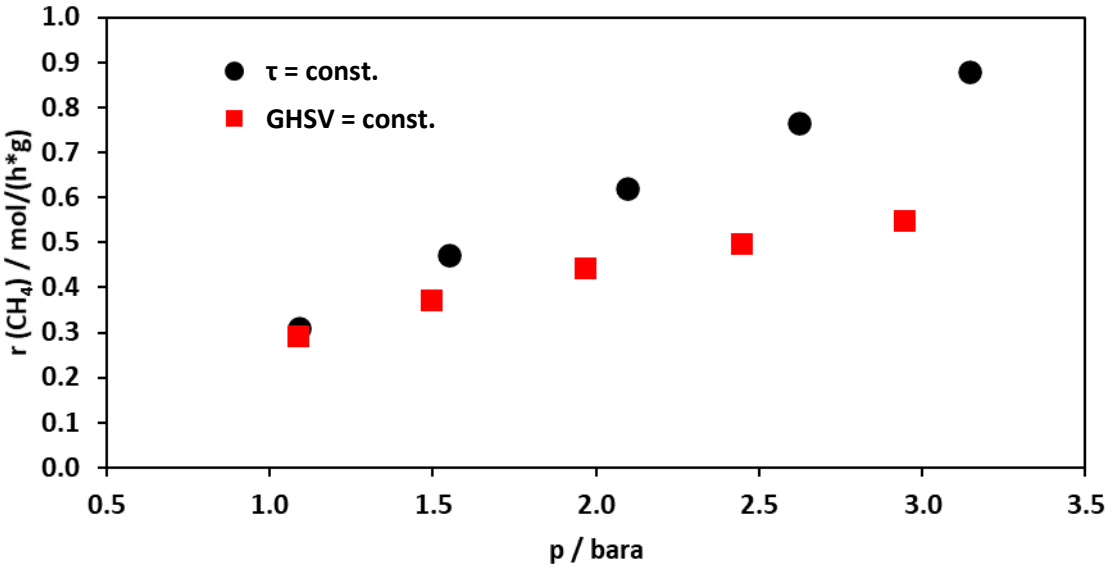


Figure 1: Reaction rate for the oxidation of CH_4 on the Mn-containing perovskite at different pressures and constant residence time (τ) or space velocity (GHSV) respectively. Conditions: y (CH_4) = 1.000 ppm, y (O_2) = 10 Vol.-%, y (H_2O) = 10 Vol.-%, N_2 balance, GHSV = 50.000 h^{-1}.

The manganese and iron containing perovskite-type catalysts reveal remarkable performance for the oxidation of HCHO and CO in synthetic as well as in the real lean exhaust gas of a stationary gas engine (not shown). By contrast, the CH_4 oxidation performance still demands significant improvement. Thus, the effect of the operation pressure on the CH_4 coverage and the resulting activity

was investigated referring to a potential pre-turbo application[5]. This is illustrated in Figure 1, where an increase in pressure did indeed result in faster reaction rates for the oxidation of CH_4. As the pressure increases from atmospheric conditions up to 3 bar, both the partial pressure and the coverage of CH_4 on the catalyst rise, resulting in accelerated reaction rates. Furthermore, elevated pressure leads to prolonged residence times at the catalyst while the space velocity is maintained, which also has a beneficial impact on the conversion of CH_4. When the flow of the reactants is adjusted with increasing pressure so that the residence time at the catalyst is constant, the reaction rate is enhanced almost linearly with rising pressure.

Moreover, the effect of the pressure on the CH_4 oxidation on the Fe-based perovskite was more systematically investigated adjusting operation pressures up to 11 bar. Figure 2 demonstrates a CH_4 conversion of 95 % at 600 °C, whereas at atmospheric pressure the conversion amounts to only 50 %.

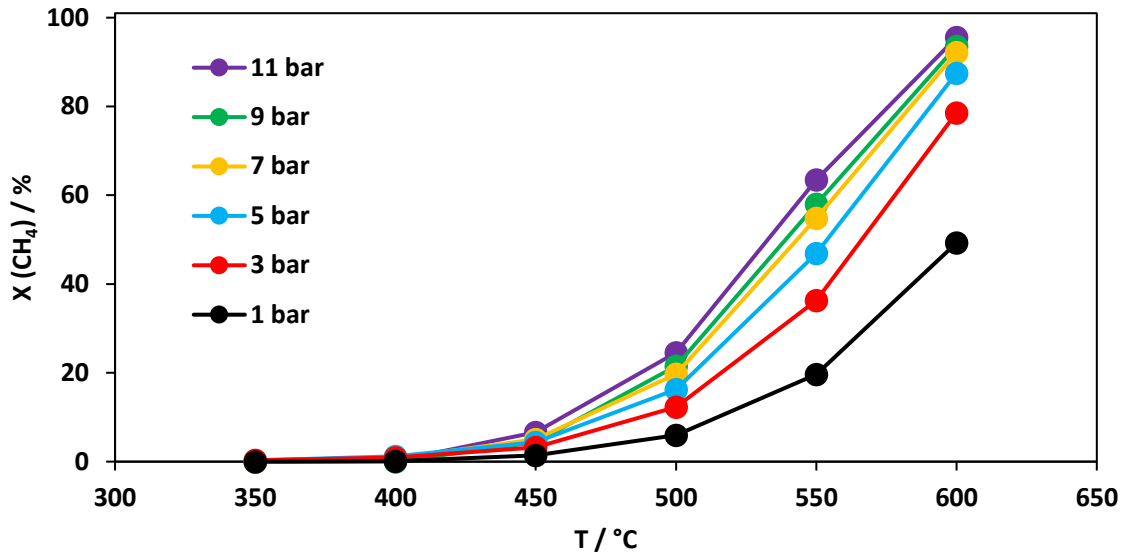


Figure 2: Conversion of CH_4 at different pressures and temperatures using the Fe-containing perovskite. Conditions: y (CH_4) = 1.000 ppm, y (O_2) = 10 Vol.-%, y (H_2O) = 10 Vol.-%, N_2 balance, GHSV = 75.000 h^{-1}.

As a consequence, the increase in pressure resulted in a drastic enhancement of the CH_4 oxidation activity suggesting that a pre-turbo application may be a promising approach to remove CH_4 from the lean exhaust of gas engines using perovskite-type catalysts [6].

References

1. S. H. Yoon, C. S. Lee, Fuel Processing Technology 92 **2011**, 5, 992–1000.
2. J. Liebetrau, J. Clemens, C. Cuhls, C. Hafermann, J. Friehe, P. Weiland, J. Daniel-Gromke, Engineering in Life Sciences 10 **2010**, 6, 595–599.
3. M. Bauer, G. Wachtmeister, MTZ worldwide 70 **2009**, 7-8, 50–57.
4. T. V. Choudhary, S. Banerjee, V. R. Choudhary, Applied Catalysis A: General 234 **2002**, 1-2, 1–23.
5. L. He, Y. Fan, J. Belletre, J. Yue, L. Luo, Renewable and Sustainable Energy Reviews 119 **2020**, article 109589.
6. M. Moser, H.-P. Walther, F. Koschany, D. Jacobsen, CIMAC Congress **2023** Busan, Paper 141.

Acknowledgements

The authors gratefully acknowledge the financial support by the FNR within the Methox project (2220NR263C)

CO_2 capture on the amino-modified mesoporous silica

Margarita Popova*[,1], Svilen Simeonov[1], Ivailo Slavchev[1], Yavor Mitrev[1], Pavletta Shestakova[1], Stela Grozdanopva[1], Ivalina Trendaflova[1]

[1] *Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, acad. G. Bonchev str., bl. 9, Sofia, Bulgaria.*

** Margarita.Popova@orgchm.bas.bg*

Significance and Relevance

The primary amine (propyl amine) and cyclic amine (piperazines) modified mesoporous silicas were successfully synthesized by a post-synthesis procedure. The used mesoporous silicas were prepared by two procedures: from rice husks as silica source without template and by sol-gel process with the application of carboxylic acids as template. High capacity for CO_2 adsorption was determined for all modified materials in dry and wet conditions and total desorption was achieved at 60 °C. The leaching of the adsorption sites was not detected. The high CO_2 uptake and straightforward preparation make the herein-reported modified silicas the CO_2 capture materials of the future.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling/ Air cleaning and combustion
Preferred presentation: Oral only

Introduction and Motivations

The increasing emission of greenhouse gases and their severe effect on the climate has come into the spotlight as a major challenge to sustainable development [1–3]. A variety of documents from the scientific community and policy-makers raise awareness and advocate for a transition towards a resource-efficient and competitive economy. The European Green Deal is a new EU strategy aiming to combat climate change by no net emissions of (GHGs) by 2050. In recent years, the adsorption of CO_2 on nanoporous materials with a high specific surface area has been the subject of extensive research. The physical characteristics and surface chemical properties of porous materials determine their CO_2 adsorption capacity, as well as their selectivity and stability in the presence of other contaminants and water vapor.

In the present study, we have developed new primary amine and cyclic amine modified mesoporous silicas that possess remarkably high CO_2 capture.

Materials and Methods

Mesoporous silicas were prepared by two synthesis procedures **(Scheme 1)**. Mesoporous silica materials were synthesized using citric acid as the template and tetraethylorthosilicate as the silica source in aqueous solution. The applied sol–gel process was performed at 30-60°C, the molar ratio of citric acid/TEOS= 1–6. The obtained mesoporous silica materials were calcined at 500 °C for 6 h, with 5 °C/min heating rate. In the second approach rice husk was subjected to acid treatment with 5% citric acid at 50°C for 3 hours. Then the rice flakes were calcined at 500 °C for 6 h, with 5 °C/min heating rate [2].

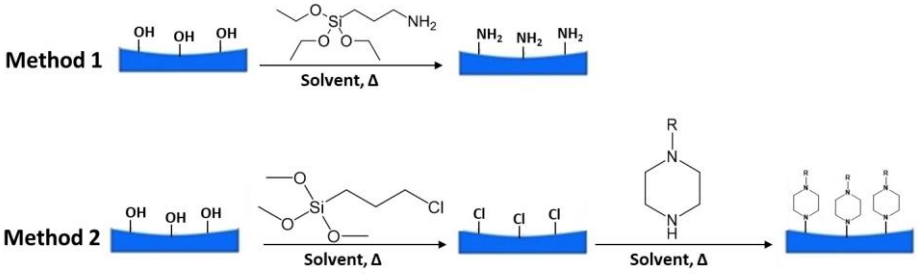


Figure 1. Scheme for synthesis of the modified mesoporous silicas

Modification of the mesoporous silicas with propylamino groups was accomplished by reaction with 3-amino-propyltriethoxysilane (APTES) in ethanol. 1 g mesoporous silica was added to 1 ml APTES in 10 ml of ethanol and was stirred at 50 °C for 5 h (Scheme 1, method 1). After that the samples were washed with several portions of solvent, and finally with water and dried at room temperature.

A total of 0.7 g of the corresponding modified mesoporous materials were suspended in 7.0 mL of dry toluene and 0.71 g of piperazine was added (Scheme 1, method 2). Then a few drops of NEt_3 were added and the reaction mixture was refluxed for 72 h. The solid phase was filtered and washed consecutively with toluene and ethanol.

The initial and modified materials were characterized by XRD (Bruker AXS Advanced X-ray Solutions GmbH, Karlsruhe, Germany), N_2 physisorption (Quantachrome instruments AUTOSORB iQ-MP-AG, Boynton Beach, FL 33426, USA), thermal analysis (STA449F5 Jupiter of NETZSCH Gerätebau GmbH (Netzsch, Germany), and solid-state NMR (Bruker Avance II+ 600 NMR spectrometer (Karlsruhe, Germany).

CO_2 adsorption experiments were performed in dynamic conditions in a flow system. The sample (0.40 g adsorbent) was dried at 150 °C for 2 h, and 3 vol.% CO_2/N_2 at a flow rate of 30 mL/min was applied for the experiments. The gas was analyzed online by GC NEXIS GC-2030 ATF with 25 m PLOT Q capillary column. The experiments for CO_2 and water vapor adsorption (3 vol.% CO_2 plus 1 vol.% water vapor) were per-formed at a flow rate of 30 mL/min. The amounts of adsorbed CO_2 and water vapor in the adsorbents were determined and used to calculate the adsorption capacity.

Results and Discussion

The propyl amine and piperazines modified mesoporous silicas were successfully synthesized by a post-synthesis procedure. The procedure for preparation of the modified mesoporous materials does not affect the structural characteristics of the initial mesoporous silicas strongly. The obtained modified mesoporous materials showed high specific surface area due to the preservation of mesoporous structure during the modification procedure. High capacity for CO_2 adsorption was determined for all modified materials in dynamic and static conditions, with some differences depending on the functional groups. The formation of chemisorbed CO_2 functionalities in the form of a bicarbonate ion (HCO_3^-) as well as the presence of physiosorbed CO_2 was evidenced by solid-state NMR.

The modification with propylamino groups and piperazine results in a high isosteric heat of adsorption due to the strong interaction between functional groups and CO_2 molecules. The highest adsorption capacity for CO_2 adsorption was determined for the piperazines modified mesoporous silica. The total CO_2 desorption from the modified materials was achieved at 60 °C. The leaching of the adsorption sites was not detected after three consecutive adsorption cycles. The high CO_2 uptake and straightforward preparation make the herein-reported modified silicas the CO_2 capture materials of the future.

References

1. J.C. Navarro, F.M. Baena-Moreno, M.A. Centeno, O.H. Laguna, J.F. Almagro, J.A. Odriozola, *Renewable and Sustainable Energy Reviews*, **2023**, *184*, 113537.
2. M. Popova, V. Mitova, M. Dimitrov, C. Rosmini, I. Tsacheva, P. Shestakova, D. Karashanova, I. Karadjova, N. Koseva, *Molecules*, **2024**, *29*, 3540.

Acknowledgements

The research was performed under the Project BG-RRP-2.011-0021-C01 with the financial support by the European Union NextGenerationEU.

Nature of Cu active centres in ferrierite based catalysts responsible for direct CO_2 transformation to platform chemicals

Julia SOBALSKA[1,2], Kinga MLEKODAJ[3], Karolina TARACH[1], Olena TYNKEVYCH[1], Dalibor KAUCKÝ[3], Jiri DEDECEK[3], Mark NEWTON[3], Kinga GÒRA-MAREK[1], and Edyta TABOR[3*]

[1]Faculty of Chemistry, Jagiellonian University in Kraków, Gronostajowa 2, 30-387 Kraków, Poland.
[2] Doctoral School of Exact and Natural Sciences, Jagiellonian University in Krakow, Łojasiewicza 11, 30-348 Krakow, Poland.
[3] J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Dolejškova 2155/3, 182 23 Prague 8, Czech Republic.
** edyta.tabor@jh-inst.cas.cz*

Significance and Relevance

Here, we present highly active copper (Cu) zeolite-based catalysts for producing acetic acid or methanol through the direct interaction of carbon dioxide (CO_2) and methane (CH_4) at 220 °C. The studied Cu-zeolites exhibit significant differences in the types and populations of copper species involved in transforming CO_2 and CH_4 into various oxygen-containing products. By combining results from in-situ spectroscopic methods (IR, UV-Vis), synchrotron techniques (XAS), and mass spectrometry, we identified the nature of the Cu active centers responsible for producing acetic acid or methanol. Our study revealed that CO_2 and CH_4 were preferentially converted into methanol by Cu-oxo species present in Cu-zeolites, whereas acetic acid production was primarily facilitated by Cu bare cations.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling and 2nd choice: Fundamental advances in understanding catalysis
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster): Oral only

Introduction and Motivations

Carbon dioxide and methane are the primary compounds contributing to Earth's escalating global warming.[1] The abundance of these gases has spurred efforts to convert them into valuable products, such as methanol and acetic acid, which serve as critical materials in industrial and chemical processes. Copper-containing zeolites represent a group of catalysts capable of effectively converting methane into methanol using O_2 in a cyclic regime.[2] Methanol is extracted from the system by using water. Moreover, studies have shown that copper species within zeolites play a significant role in CH_4/CO_2 interactions, leading to the formation of acetic acid. However, the nature of the active copper centers and the mechanism of CO_2/CH_4 transformation remain subjects of ongoing debate.

This paper presents research on the conversion of methane and carbon dioxide into acetic acid and methanol over Cu-FER zeolites, using advanced operando spectroscopic techniques (UV-Vis, FTIR, XAS, and mass spectrometry). The study aims to experimentally analyze copper species within FER zeolites, examining their roles in the selective formation of CH_3COOH or CH_3OH from the CO_2/CH_4 reaction mixture. The results obtained could significantly contribute to the design of catalysts dedicated to processing CO_2 and CH_4 into value-added products.

Results and Discussion

Two Cu-FER samples differing in the types of copper species were prepared by ion-exchange procedure. The sample with low copper loading (Cu/Al ratio 0.06) was denoted as Cu-FER-L and high loaded Cu-FER with (Cu/Al ratio 0.4) was denoted as Cu-FER-H. Analysis combining FTIR, UV-Vis, and XAS results confirmed the presence of a high fraction of Cu(II) species and a smaller population of Cu(I) species in both samples. In Cu-FER-L, copper is primarily located in cationic positions, whereas the copper-rich Cu-FER-H contains copper species in both cationic positions and various forms of Cu-oxo species. The evaluation of CH_4 and CO_2 interaction products on Cu-FER catalysts, monitored in the

temperature range of 25–450 °C using coupled FTIR and mass spectrometry techniques, allowed for the detection of reaction products adsorbed on the catalyst surface (via FTIR) as well as the composition of the gas phase (via mass spectrometry). The FTIR spectra of Cu-FER-L confirmed acetic acid formation at temperatures above 200°C, evidenced by the appearance of new bands at 1580 and 1490 cm^{-1} (indicative of acetic acid) and 1334 cm^{-1} (associated with the CH_3 group). Detailed analysis of the FTIR spectra revealed that acetic acid production occurs in two stages, at 210°C and 280°C. The FTIR spectra of Cu-FER-H also showed the formation of bands characteristic of acetic acid following CO_2/CH_4 interaction. Furthermore, in both samples, the presence of acetic acid among the reaction products was confirmed by the detection of an m/z = 60 signal.

To characterize the catalytic behavior of Cu-FER-L and Cu-FER-H in CO_2 and CH_4 transformation, the reaction was carried out at a constant temperature of 200 °C. Figure 1 shows the time dependence of FTIR spectra (upper part) in a top-down projection, alongside the evolution (bottom part) of mass spectrometry signals for acetic acid (m/z = 60), carbon dioxide (m/z = 44), methanol (m/z = 31), water (m/z = 18), and methane (m/z = 16). For the Cu-FER-L zeolite, bands corresponding to acetate ions (1580–90 and 1490 cm^{-1}) and CH_3 groups (1334 cm^{-1}) appeared within the first few minutes, with product accumulation on the surface intensifying after 30 minutes. From that point, the increasing intensities of bands associated with acetates and water molecules (1615 cm^{-1}) were accompanied by a marked decrease in CO_2 (2350 cm^{-1}) and CH_4 gas-phase bands (3100–2800 cm^{-1}). The m/z = 60 signal over time indicates acetic acid generation for 60 minutes, after which production attenuates, corresponding to a substantial accumulation of acetate ions on the catalyst surface. Acetic acid production is also associated with the formation of methanol and water, likely resulting from the oxidation of CH_4 by copper(II) oxo-forms. As the reaction progresses, methanol and water production decrease, probably due to the strong adsorption of acetate ions on active copper sites. In the case of Cu-FER-H zeolite, with a high content of copper(II) oxo-species, only methanol and water are produced in large quantities, while acetic acid formation remains minimal. This finding suggests that the presence of copper(II) oxo-forms is unfavorable for acetic acid production, as these centers tend to consume methane by oxidizing it to methanol. Integration of the m/z signals for acetic acid over the entire reaction duration revealed that acetic acid was formed with 20% efficiency in the Cu-FER-L catalyst, compared to 3.5% for Cu-FER-H.

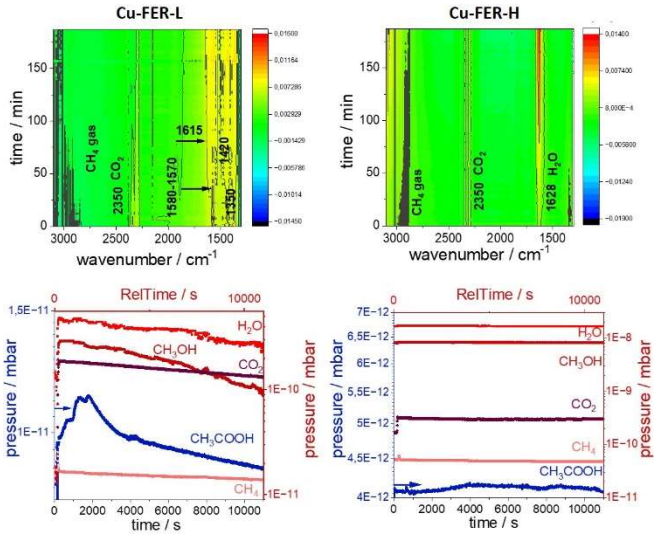


Figure 1. (Upper part) Top-down projection of difference spectra. (Bottom part) Time dependence of the signal intensity (ion currents) of CH_3COOH, CO_2, CH_3OH, H_2O, and CH_4.

These findings clearly indicate that Cu cations are primarily responsible for acetic acid production, while Cu-oxo species facilitate the transformation of CO_2 and CH_4 into methanol in the catalytic regime.

References

1. E. M Wilcox, G. W. Roberts, James J Spivey, *Catal. Today* **2003**, *1-2*, 83.
2. J. Wieser, A. J. Knorpp, D. C. Stoian, P. Rzepka, M. A. Newton, J. A. van Bokhoven, *Angew. Chem. Int. Ed.*, **2023**, *62*, e202305140.

Acknowledgements

The authors thank the Czech Science Foundation #24-14387L and the National Science Centre, Poland, 2022/47/I/ST4/00607 for the financial support.

$Ag/Ce_{1-x}Mn_xO_2$ Catalysts for Soot Oxidation: Role of Ce/Mn Molar Ratio

Ekaterina S. L'vova,[1] Tamara S. Kharlamova,[1] Maria V. Grabchenko,[1] Olga V. Vodyankina,*[1] Eleonora La Greca,[2] and Leonarda F. Liotta*[2]

[1] *Tomsk State University, 36 Lenin Ave., Tomsk, 634050, Russian Federation*
[2] *CNR, ISMN, Via Ugo La Malfa 153, 90146-Palermo, Italy*

** leonardafrancesca.liotta@cnr.it*

Significance and Relevance

This study highlights the development of Ag/CeO_2, Ag/MnO_x, and $Ag/CeMnO_x$ catalysts prepared via the citrate sol-gel method, focusing on their efficacy in soot oxidation. The novel nanodomain structure in $CeMnO_x$, influenced by the Ce/Mn ratio, enhances catalytic activity and stability, particularly at a 1:1 ratio, which prevents CeO_2 sintering. The catalysts demonstrate selective soot oxidation to CO_2 at relatively low temperatures (<500°C for powders and <600°C for monoliths), showcasing their practical potential. Additionally, the findings reveal NO inhibitory effects on oxidation, mitigated by CO in $NO+O_2$ mixtures, offering valuable insights for emission control technologies.

Preferred and 2nd choice for the topic: Automotive and stationary emission control; Air cleaning and combustion.
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Diesel engines, known for their strong power performance and high fuel efficiency, are considered a promising power source for light vehicles, which have predominantly relied on gasoline engines. However, a widespread adoption of diesel engines is hindered by significant emission issues, particularly the release of particulate matter (PM) mainly composed of soot. The use of catalytic filters, specifically diesel particulate filters (DPFs), which trap and oxidize soot effectively reducing its harmful impact by significantly lowering the soot oxidation temperature. CeO_2 is highly regarded for its exceptional catalytic activity and redox behavior. [1] Similarly, MnO_x is widely utilized in oxidation and reduction reactions, thanks to its multivalent oxidation states (mainly Mn^{2+}, Mn^{3+}, and Mn^{4+}) and the high mobility of lattice oxygen.[2] When combined, MnO_x-CeO_2 catalysts demonstrate superior catalytic activity significantly lowering the ignition temperature for soot oxidation due to the synergistic effect between the two metal oxides. [3] Furthermore, the addition of silver to the CeO_2 and MnO_x catalyst significantly boosts its reactivity for soot oxidation. [4] The aim of this study was to evaluate the performance of the $Ag/CeMnO_x$ catalysts in soot combustion under tight and loose contact conditions flowing 10 vol.% O_2/He as well as in the presence of NO and NO-CO.

Materials and Methods

Oxide supports were prepared by the citrate sol-gel method, using $Ce(NO_3)_3 \cdot 6H_2O$ and $Mn(NO_3)_2 \cdot 6H_2O$ as precursors in Ce/Mn molar ratios equal to 1/3, 1/1 or 3/1, after drying were calcined at 500°C. Ag catalysts (1 wt.%) were prepared by wet impregnation using $Ag(NH_3)_2$ and were calcined at 500 °C. The resulting samples were labeled as Ag/Ce, Ag/Mn and Ag/1Ce3Mn, Ag/1Ce1Mn and Ag/3Ce1Mn. Portions of the catalysts were treated in oven at 650°C for 12 h in order to simulate thermal aging.
Characterization by XRD, N_2 physisorption, XRF, Raman, SEM and TEM techniques was performed. Catalytic tests were carried out under tight and loose contact conditions in temperature-programmed

reaction (TPR) mode, under a flow of 10 vol.% O_2/He, 10 vol.% O_2, 0.1 vol.% NO/He, or 10 vol.% O_2, 0.1 vol.% NO, 1.25 vol.% CO/He.

Results and Discussion

Fig. 1a shows that in the presence of the supported Ag catalysts the temperature of soot oxidation significantly decreased with respect to the not catalyzed process. Moreover, in the presence of catalysts soot was fully oxidized to CO_2, while without any catalyst CO and CO_2 are formed. The Ag/Mn and Ag/1Ce3Mn samples demonstrated the lowest activity (~50% of soot conversion was achieved at around 500°C). A further increase in the Ce content in the oxide matrix resulted in the improvement of the catalyst activity, the Ag/Ce sample showing the highest activity (Tmax=448°C). Thermal aging at 650°C for 12 h lead to a significant deactivation of the Ag/Ce (aged) (Tmax=529°C) due to a strong decrease of the specific surface area and an increase in the crystallites size. The Tmax of soot oxidation over Ag/3Ce1Mn (aged) increased to 500°C (ΔTmax=37° C), while the Ag/1Ce1Mn (aged) appeared the most stable with the best oxidation performance (Tmax=465°C, ΔTmax=7° C), (Fig. 1b).

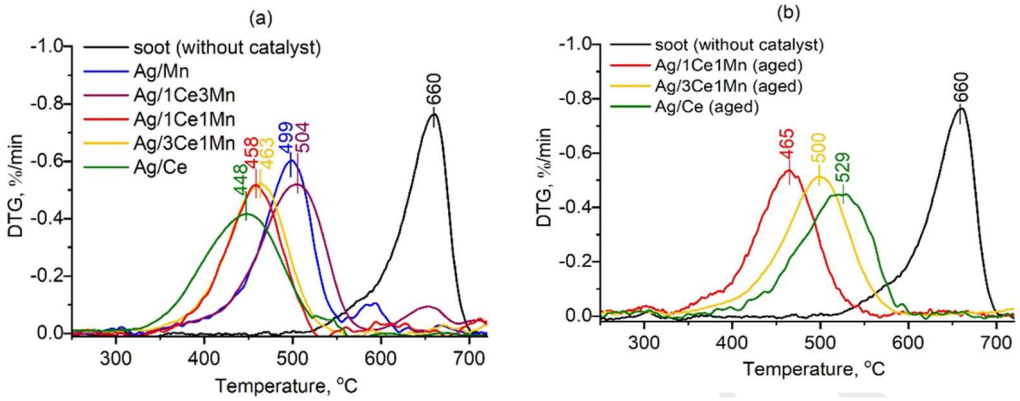


Figure 1. Soot oxidation activity versus temperature for fresh Ag supported catalysts (a) and those aged at 650 °C for 12 h (b).

References

1. A. Setiabudi, J. Chen, G. Mul, M. Makkee, J.A. Moulijn, *Applied Catalysis B Environ*mental **2004**, 51(1), 9-19
2. R. Mane, H. Kim, K. Han, K.-J. Kim, S. S. Lee, H.-S. Roh, C. Lee, Y. Jeon, *Fuel* **2023**, 346, 128287
3. X. Lin, S. Li, H. He, Z. Wu, J. Wu, L. Chen, D. Ye, M. Fu, *Applied Catalysis B Environ*mental **2018**, 223, 91-102.
4. M.V. Grabchenko, G.V. Mamontov, V.I. Zaikovskii, V. La Parola, L.F. Liotta, O.V. Vodyankina, *Applied Catalysis B Environ*mental **2020**, 260, 118148

Acknowledgements

This work was supported by the Russian Science Foundation, Grant No. 19-73-30026. The authors acknowledge A.G. Golubovskaya (Tomsk State University) for SEM study.

Maximizing the efficiency of Ir-based oxygen evolution electrocatalysts through Ni doping

Anna Giulia Cardone[1,2], Fabrizio Pirri[1,2], Marco Etzi[*,1]

[1] *Istituto Italiano di Tecnologia, Center for Sustainable Future Technologies, Via Livorno 60, 10144, Torino, Italy.*
[2] *Politecnico di Torino, Dept. of Applied Science and Technology, Corso Duca degli Abruzzi 24, 10129, Torino, Italy.*
** marco.etzi@iit.it*

Significance and Relevance

This study presents novel Ir-TM (transition metal) catalysts for the Oxygen Evolution Reaction (OER) in acidic media, aiming to reduce the use of noble metals while enhancing performance. The key result is the higher catalytic activity of the mixed Ir-Ni alloy compared to pure Ir and IrO_2, attributed to changes in the crystalline and/or electronic structure and electrochemical surface area. This work provides a path toward more efficient and cost-effective OER catalysts for Proton-Exchange Membrane Electrolyzers (PEMs), addressing the scalability and sustainability challenges.

Preferred and 2nd choice for the topic:

1) *H2 storage and transportation, green H_2 production, hydrogen vectors;*
2) *Sustainable and clean energy production and transport.*

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The Oxygen Evolution Reaction (OER) is regarded as the bottleneck in electrochemical water splitting due to its slow kinetics. Currently, IrO_2 is the only material that offers the necessary activity and stability to function as an OER catalyst in the acidic environment of Proton Exchange Membrane (PEM) electrolyzers. For large-scale implementation, it is crucial to reduce the loading of noble metals in the catalyst composition as much as possible.[1] Introducing other transition metals, in the composition offers several possibilities to boost the performance of OER catalysts by changing their crystalline and electronic structure, as shown in our previous study on mixed Ir-Mn catalysts.[2]

Materials and Methods

Catalysts were prepared by thermal decomposition or by an innovative microwave synthesis. The crystalline structure, the morphology and composition, and the electronic structure were analyzed by X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FE-SEM), Energy Dispersive X-Ray Spectroscopy (EDX), and X-Ray Photoelectron Spectroscopy (XPS). The electrocatalysts were tested in a three-electrode cell using an acidic electrolyte to assess their activity and stability.

Results and Discussion

Microwave synthesis is a fast and scalable process for the fabrication of electrocatalysts. As opposed to thermally prepared materials, which are mainly in the form of oxides,[3] this synthesis led to the formation of metallic alloys.

Both doped and undoped Ir-based catalysts have higher catalytic activity as compared to a commercial IrO_2 catalyst. Doping Ir with Ni further increased the catalytic activity, resulting in higher current densities in Linear Sweep Voltammetry (LSV) (Figure 1) and lower Tafel slope. The higher activity of mixed catalysts is maintained after a stability test; undoped and doped Ir-Ni catalysts exhibit similar trends of current densities but they were shifted to higher values for the mixed catalysts (Figure 2). In-depth characterization of the fresh and used catalyst evidenced differences in morphology and composition.

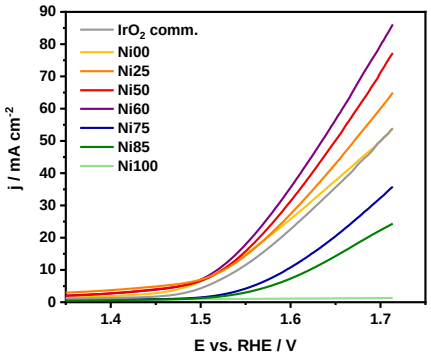


Figure 1. Linear Sweep Voltammetry of the catalysts.

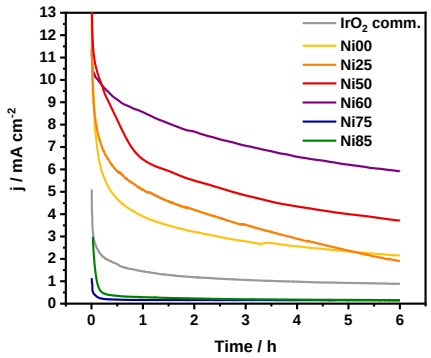


Figure 2. Chronoamperometry at E = 1.6 V vs. RHE.

References

(1) Vesborg, P. C. K.; Jaramillo, T. F. Addressing the Terawatt Challenge: Scalability in the Supply of Chemical Elements for Renewable Energy. *RSC Adv.* **2012**, *2* (21), 7933–7947. https://doi.org/10.1039/c2ra20839c.

(2) Etzi Coller Pascuzzi, M.; Hofmann, J. P.; Hensen, E. J. M. Promoting Oxygen Evolution of IrO2 in Acid Electrolyte by Mn. *Electrochim. Acta* **2021**, *366*, 137448. https://doi.org/10.1016/j.electacta.2020.137448.

(3) Etzi Coller Pascuzzi, M.; Goryachev, A.; Hofmann, J. P.; Hensen, E. J. M. Mn Promotion of Rutile TiO<inf>2</Inf>-RuO<inf>2</Inf> Anodes for Water Oxidation in Acidic Media. *Appl. Catal. B Environ.* **2020**, *261*. https://doi.org/10.1016/j.apcatb.2019.118225.

Acknowledgments

The authors acknowledge the Project “Network 4 Energy Sustainable Transition—NEST”, Spoke 4, Project code PE0000021, funded under the National Recovery and Resilience Plan (NRRP), Mission 4, Component 2, Investment 1.3— Call for tender No. 1561 of 11.10.2022 of Ministero dell’Universita` e della Ricerca (MUR); funded by the European Union—NextGenerationEU.

Catalytic methane cracking over amorphous and regular structured carbons

Enrico CATIZZONE, Daniela COZZA, Girolamo GIORDANO*, Massimo MIGLIORI,
Chemical Engineering Catalysis and Sustainable Processes Laboratory, University of Calabria, Rende, Italy.
.
** ggiordaunical@yahoo.it*

Significance and Relevance

Carbons with amorphous (activated carbons, biochar) and regular structure (Zeolite templated Carbons) are compared for the first time as catalysts for the methane cracking for the selective production of hydrogen. The activity of carbons is not related to inorganic impurities but to surface features, not related to the presence of reducible functional groups, i.e. oxygen-based. The deactivation behavior strongly depend on the carbon type and reaction temperature. Zeolite templated carbons show the highest hydrogen productivity with a good stability.

Introduction and Motivations

Cracking of methane, especially at low temperature, can be considered a promising technology to produce turquoise hydrogen. Nickel-based catalysts are the most investigated, although a rapid deactivation is observed due to the deposition of graphitic carbon[1]. In this concern, catalysis with nanocarbons represents an interesting alternative due to the possibility to promote a carbon-over-carbon growth[2]. Epitaxial growth would make stable the process with the opportunity to produce both hydrogen and high-quality carbons as key products.

Materials and Methods

Two commercial activated carbons, named SICAV SV50 (SICAV S.p.A) and G-BAC (Kureha Group), one biochar (derived from pyrolysis of olive prunings) and one Zeolite Templated Carbon (ZTC), are used as catalysts for methane cracking. Methane cracking is carried out in a lab-scale tubular reactor, feeding a methane/nitrogen feed with a 20 vol.% of methane. The reaction temperature is set at 700 °C, 800 °C or 900 °C and the space velocity is ranged from 240 to 1440 $NL_{CH4}/(h\ kg_{cat})$. Among the investigated materials, the G-BAC activated carbon is characterized by a very low ash content (lower than 500 ppm). ZTC sample is synthesised by chemical vapor deposition/polymerization of ethylene at 800 °C[3].

Results and Discussion

All the samples exhibit a selectivity towards hydrogen close to the unity, under the investigated conditions. The main catalytic results as a function of reaction temperature and gas hourly space velocity are reported in Figure 1. The deactivation behavior strongly depend on both temperature and catalyst type. At 900 °C, a rapid deactivation is observed for biochar, while activated carbons seems to shows a more gradual deactivation, and ZTC is the only sample showing a conversion higher than 10% at the end of the test. Lowering the temperature to 800 °C, deactivation is retarded, albeit biochar slower but completely deactivates during the test. Pre-treatment with hydrogen (results not shown here) does not significantly impacts on the catalytic performances, although the samples show an important hydrogen consumption during temperature programmed reduction measurements. This result indicate that the hydrogen produced during the reaction does not alter the catalytic features, or the reducible functionalities are not responsible for the catalysis.

The temperature of 800 °C is surely the most suitable for hydrogen production, this also favored at lower gas hourly space velocity. Under the optimal conditions, ZTC exhibits the highest hydrogen productivity, which is higher than 700 NL of hydrogen produced for each Nm^3 of methane fed to the reactor, as reported in Figure 2.

Reaction mechanism and the identification of the active sites in carbon-based materials remain open challenges.

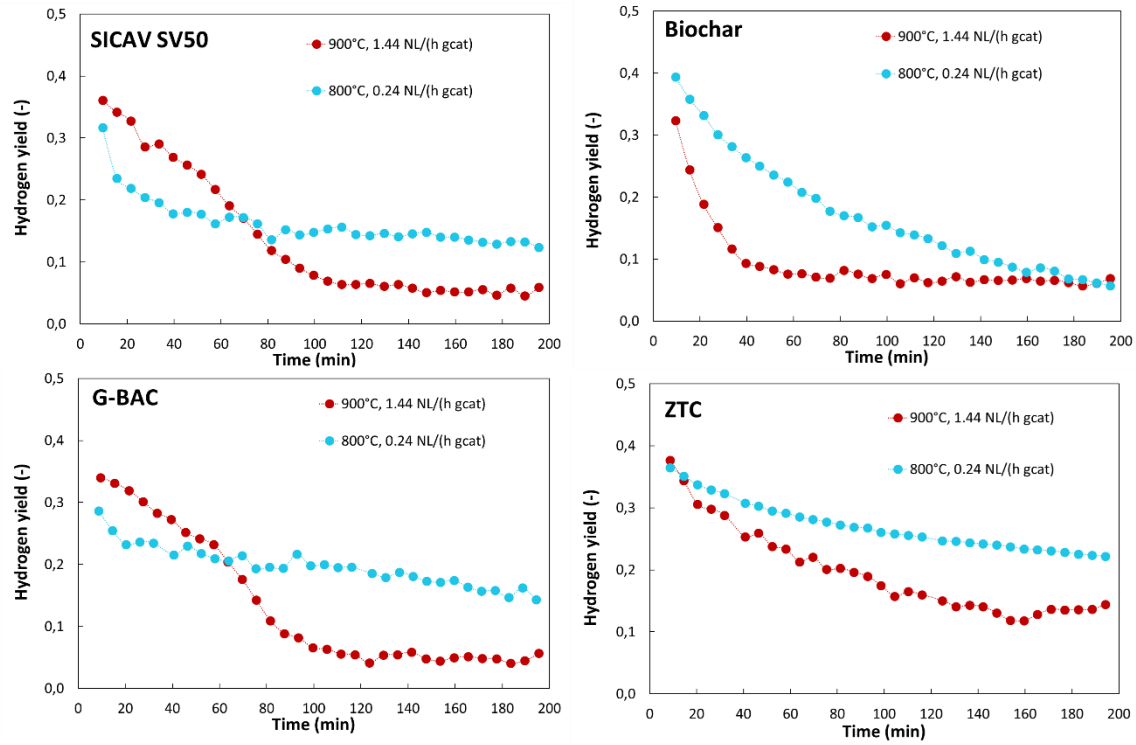


Figure 1 – Time on Stream tests of the investigated materials at different space velocity and temperature.

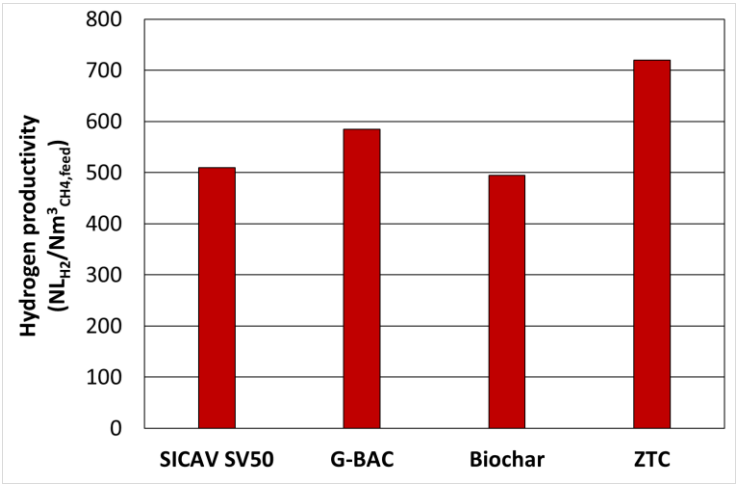


Figure 2 – Hydrogen productivity, 2 h Time-On-Stream, 800 °C and GHSV=240 NL/h/kg.

References

1. M. McConnachie, M. Konarova, S. Smart, *Int. J. Hydrogen Energy* **2023**, *48(66)*, 25660.
2. S.M.R. Mirkarimi, S. bensaid, V. Negro, D. Chiaramonti, *Renew. Sus. Energy Rev.* **2023**, *187*, 2113747.
3. A. Policiccio, G. Conte, R. G. Agostino, G. Desiderio, G. Papanikolaou, P. Lanzafame, D. Cozza, G. Giordano, M. Migliori, *Carbon* **2023**, *201*, 991.

Acknowledgements

This work was funded by the Next Generation EU - Italian NRRP, Mission 2, Component 2, Investment 3.5, - project MECCA - H2 verde da cracking del bioMEtano tramite una tecnologia innovativa basata su plasma non-termico e Catalisi con nanoCArboni, n. RSH2A_000002. This work reflects only the authors' views and opinions, neither the Ministry for University and Research nor the European Commission can be considered responsible for them.

Novel APPJ-thermal hybrid system for methane decomposition

Francesco Pio ABRAMO*[1], Muhammed SABIR[1], Palmarita DEMORO[1], Siglinda PERATHONER, Gabriele CENTI[1], Ruben BARTALI[2], Alireza GANJOVI[2], Salvatore ABATE[1]

[1]*University of Messina, Department of ChiBioFarAm (Industrial Chemistry), V.le F. Stagno d'Alcontres, Messina, Italy.*

[2] *Fondazione Bruno Kessler, Via Sommarive 18, Trento, Italy.*

** francescopio.abramo@unime.it*

Significance and Relevance

The combination of an Atmospheric Pressure Plasma Jet (APPJ) with external heating represents a novel hybrid system for decomposing (bio)methane into hydrogen and carbon. As methane splitting occurs at high temperatures even with a catalyst (≥900°C), using cold plasma could be of significant relevance for the activation of CH_4 at room temperature. Consequently, a lower temperature (≤ 750°C) would be required in the subsequent thermal step, thereby facilitating the development of a novel CO_2-free hydrogen production process that is more commercially viable.

Introduction and Motivations

A low-carbon hydrogen production is one of the hot topics of industrial research thank to its several use from chemicals production to energy vector[1], and its use will reach 150 Mt by 2030 making it a high demand commodity.[2]

Decomposition of (bio)methane is an attractive route among low-carbon hydrogen production technologies because it requires approximately 87% lower energy than water electrolysis, but its kinetic needs high temperature, making this process energy extensive. Moreover, inevitable amorphous carbon produced, and soot deposition decreases catalyst activity by time and requires post-reaction separation and purification steps, increasing the overall cost of the process. To cope with the limitations mentioned, in this work a plasma and thermal hybrid system is proposed as financially viable solutions on an industrial scale.

Materials and Methods

The APPJ reactor consists of an inner metallic pipeline acting as AC high-voltage electrode and a coaxially placed quartz tube. Three different configurations (figure 1) without (A) or with ground electrode were tested, consisting of a simple clamp (B), or aluminum foil (C) wrapped around a quartz tube. In the second stage, activated CH_4 flows inside the furnace, where bulk reaction temperature was controlled from 600°C to 750°C. The distance between plasma and thermal zones varied in order to study the effect on conversion and selectivity through hydrogen, carbon, and C2-C3 impurities. For the same reason carbon-based catalysts, commonly used for only thermal decomposition of methane, were placed inside the thermal stage. Optical emission spectroscopy (OES) was used to analyze species formed within the plasma discharge and to determine the physical-chemical parameter as the level of electronic temperature and concentration of activated species.

Results and Discussion

At a fixed plasma power of 20W and a distance of 14.5cm between the two stages, the conversion rate was raised from 1.5% to 3.8% when plasma was combined with the thermal stage in configuration A at a temperature of 600°C. Similarly, results were witnessed in the case of configurations B and C, although there was a less marked increase. A further conversion of 12.8% was observed when there was no distance between the two stages, using configuration A. Moreover, it was demonstrated that no conversion occurred when only the thermal stage was used at the same temperature, which serves to substantiate the beneficial effect of coupling APPJ and thermal methane decomposition. The observed increase in conversion can be attributed to the activation of CH_4 molecules by the energetic plasma environment in the first stage, which provides abundant CH_x-based radicals, as sustained by the plasma peaks determined by OES analysis.[3] Additionally, the short lifetime of active CH_4 explains

the increased conversion when there is no distance between the two stages, allowing for a higher decomposition when plasma is generated directly inside the thermal zone. The presence of a high concentration of H radicals also explains the highest selectivity to hydrogen (~40%) across all three configurations, with ethane, solid carbon, ethylene, and a minor amount of propane and propylene as the subsequent products. These findings contribute to a deeper understanding of the plasma thermal hybrid system and provide a comprehensive account of its behavior.

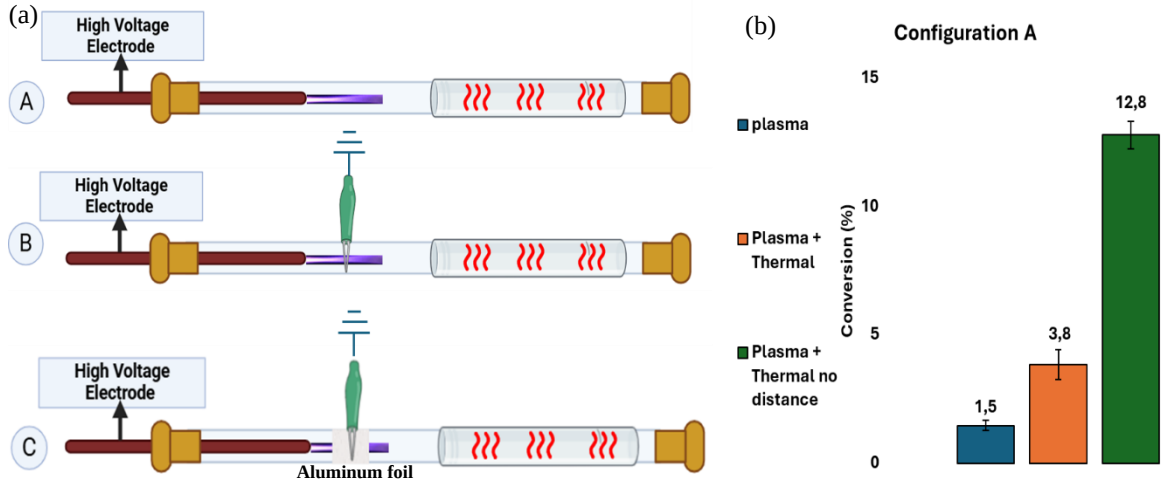


Figure 1 (a) APPJ configurations without (A), or with clamp (B) and aluminum foil (C) as a ground electrode and (b) CH_4 conversion in configuration A.

References

1 S. Evro, B. A. Oni and O. S. Tomomewo, *Int. J. Hydrogen Energy*, **2024**, *78*, 1449–1467.

2 International Energy Agency, Report, **2024**.

3 H. Bai, B. Huang, Y. Liu, C. Zhang and T. Shao, *J. Phys. D. Appl. Phys.*, **2021**, *42*.

Acknowledgements

The project is funded by:

- H_2 verde da cracking del bioMEtano tramite plasma non-termico e Catalisi con nanoCArboni (MECCA) under the grant No. RSH2A_000002
- ERC Grant “Surface-Confined Fast Modulated Plasma for Process and Energy Intensification" (SCOPE) under the grant No. 810182

SHORT ORAL ABSTRACTS



Transition metals over C-based materials: unraveling performances and challenges

Sina E. Atakoohi[1], Elena Spennati[1,2], Paola Riani[2,3], Gabriella Garbarino[1,2,*]
[1]*University of Genova, DICCA Dept., Genova, 16145 (Italy)*
[2]*INSTM, UDR Genova, 16146 (Italy)*
[3]*University of Genova, DCCI Dept., Genova, 16146 (Italy)*

** gabriella.garbarino@unige.it*

Significance and Relevance

In the pursuit of carbon neutrality, the conversion of CO_2 to methane or even to syngas will be a pivotal process. This study aims to examine the catalytic performance of cutting-edge carbon-based catalysts, as an alternative to conventional alumina-based ones, in CO_2 hydrogenation and dry reforming reactions. The findings will offer a comprehensive insight into the influence of the support and its impurities on the selectivity of different products.

Preferred and 2nd choice for the topic: Fundamental advances in understanding catalysis, Circular economy
Preferred presentation: *Oral*

Introduction and Motivations

The capture and utilization of CO_2 are regarded as a promising strategy for mitigating the environmental challenges confronting the globe and for achieving carbon neutrality by 2050[1]. In order to reduce CO_2 emissions, in particular those arising from the power sector, the use of hydrogenation reactions to produce CH_4 or CO through Sabatier's or reverse water gas shift (rWGS) reactions appears to be a promising strategy. Furthermore, the production of syngas through dry reforming represents another un-exploited reaction. In general, formulated metal supported catalysts suffer deactivation due to coke deposition and/or particle sintering[2-5], thus hindering the exploitation at the industrial scale. For these reasons, the development of new catalysts is a challenge. Among the potential options, carbon-based materials are well-suited as catalyst supports due to their low cost, natural abundance, high stability in both acidic and basic conditions, and high catalytic activity in several reactions[6-7]. In this study, carbon-based supports, including commercial graphene nanoplatelet (Gnp), homemade Gnp prepared via the molten salt method, and reduced graphene oxide, were employed as a support for Ni, Co, and/or Ru-based catalysts for CO_2 hydrogenation and dry reforming reactions.

Materials and Methods

The catalysts, with a total metal loading of 2 and 5 wt.% for Ni and Co-based ones and 0.5 wt.% for Ru-based ones, were supported on commercial (C) or homemade (H) graphene nanoplatelets (Gnp) and reduced graphene oxide (rGO). They were prepared by incipient wetness impregnation using ethanol as the solvent. The prepared materials were characterized by a range of techniques, including vibrational spectroscopies, XRD, FE-SEM, SEM-EDXS, and TEM. Prior to testing in Sabatier's, rWGS, and dry reforming reactions, an in-situ drying-reducing process was investigated and performed. A novel method for determining carbon loss during drying-reduction tests was developed and performed using online IR spectroscopy.

Results and Discussion

In Figure 1, CO_2 hydrogenation catalytic performances with the prepared catalysts are shown in terms of yield to methane and CO. At all temperatures investigated, the carbon-based catalysts exhibited a higher catalytic performance in rWGS reaction than Sabatier's one. It is noteworthy that the cobalt catalyst exhibited enhanced catalytic activity at low temperatures ($T < 632$ K), with a CO yield of 38% at 632 K. The Ni and Ru-based catalyst supported on homemade Gnp demonstrated

superior catalytic activity in terms of CO production compared to those supported on commercial ones. Conversely, catalysts supported on rGO demonstrated limited catalytic activity in both reactions. The characterization of exhaust catalysts revealed partial graphitization of Gnp and the presence of distributed Ru- and Ni-based particles (with an average dimension of 5-10 and 10-25 nm, respectively), even though sulfur impurities (0.5 wt%) appears upon in-depth investigations.

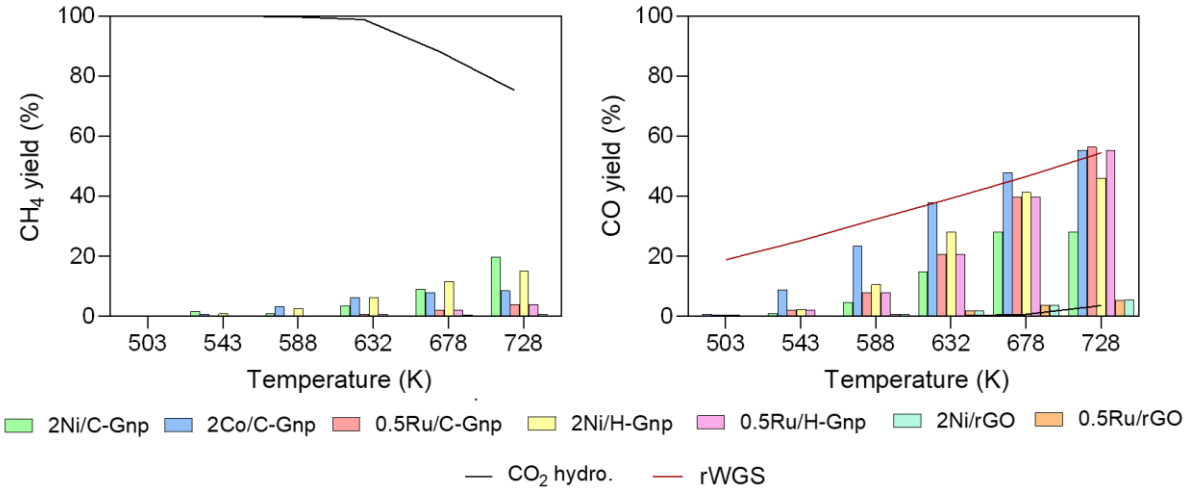


Figure 1. CO_2 hydrogenation catalytic performances with carbon-based catalysts

Co- and Ni-based catalysts showed promising results in dry reforming reaction obtaining a CO yield above 80% in the temperature range 773-973 K and at present time characterization of the exhaust materials is undergoing.

References

1. IEA.org /reports/global-energy-review-2021/CO_2-emissions.
2. G. Garbarino, P. Riani, L. Magistri, G. Busca, *Int. J. Hydrogen En.* **2014**, 39, 11557-11565.
3. G. Garbarino, D. Belotti, P. Riani, L. Magistri, G. Busca, *Int. J. Hydrogen En.* **2015**, 40, 9171-9182
4. G. Garbarino, C. Wang, T. Cavattoni, E. Finocchio, P. Riani, M. Flytzani-Stephanopoulos, G. Busca, *Appl. Catal. B: Environ* **2019**, 248, 286-297.
5. P. Riani, I. Valsamakis, T. Cavattoni, V. Sanchez Escribano, G. Busca, G. Garbarino, *Appl. Catal. B: Environ.* **2021**, 284, 119696.
6. M. B. Gawande, P. Fornasiero, R. Zbořil, *ACS Catal.* **2020**, 10, 2231–2259.
7. J. Wu, T. Sharifi, Y. Gao, T. Zhang, P. M. Ajayan, *Adv. Mater.* **2019**, 31, 1–24.

Acknowledgements

G.G. and E.S. acknowledge the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3—Call for tender No. 1561 of 11.10.2022 of Ministero dell'Università e della Ricerca (MUR); funded by the European Union—NextGenerationEU project title "Network 4 Energy Sustainable Transition—NEST" (project code PE0000021).

Operando-FTIR investigation of bifunctional Pt or Pd,Fe-HMOR catalyst for simultaneous abatement of NO_x and N_2O by CH_4

Michele LEONE[*,1], Chiara CAPONERA[1], Daniela PIETROGIACOMI[1], Simone MORPURGO[1], Maria Cristina CAMPA[2]
[1]*Chemistry Department, Sapienza University of Rome, 00185 Rome, Italy.*
[2] *ISMN-CNR, c/o Chemistry Department, Sapienza University of Rome, 00185 Rome, Italy.*
[*]*michele.leone@uniroma1.it*

Significance and Relevance

The simultaneous removal of NO_x and N_2O is performed by a bifunctional catalyst in which Pt or Pd metal particles located outside MOR channels abate NO_x and Fe^{n+} ions located at exchanging sites inside the MOR channels abate N_2O. The reductants/oxidants ratio in the reactant mixture, $CH_4/(NO+N_2O+O_2)$, affects the oxygen transfer processes at the active sites, determining their redox states. The formation of adsorbed NO_y species that can deactivate the catalyst occurs on oxidized sites. The formation of adsorbed NH_4^+ species probes the Pt or Pd metal nanoparticles formation. The different interaction strength of cations with MOR exchanging sites, weak for Pt and Pd ions and strong for Fe ones, leads to active sites in different locations, aggregated noble-metal nanoparticles on external surface and Fe ions confined inside the channels, guaranteeing simultaneous and nearly independent pathways for the two abatements.

Introduction and Motivations

The primary objective of environmental catalysis is to create innovative processes that reduce atmospheric pollutant emissions from both mobile and stationary sources. Since noble metals are highly effective catalysts for NOx reduction using hydrocarbons[1], and iron-containing zeolites are widely utilized for N_2O decomposition or reduction in nitric acid production[2], we focused on bimetallic Pt,Fe-HMOR or Pd,Fe-HMOR zeolites. These catalysts showed potential for reducing simultaneously the NO_x and N_2O emissions in a single catalytic bed using CH_4 as the reductant (SCRsim). The synergistic interactions between the active metals was investigated by examining the surface intermediates formed during reactions with varying reactant mixtures.

Materials and Methods

Pt,Fe-HMOR and Pd,Fe-HMOR catalysts were prepared using a commercial HMOR (Si/Al=9.2, Tosoh Corp.) through a two-step procedure. This involved ion-exchange with aqueous solutions of noble metal salts, followed by wet impregnation with $Fe(NO_3)_3$ solution corresponding to 30% of Fe^{3+}-exchange degree. Catalytic activity was evaluated under steady-state conditions using 100 mg of catalyst in a plug flow reactor connected to a flow system at atmospheric pressure, with gas-chromatographic (GC) gas-phase analyses. *Operando*-FTIR studies were carried out on a catalyst wafer (10 mg/cm²) placed in a stainless-steel IR reactor integrated into the flow apparatus. FTIR spectra were recorded during gas flow at temperatures up to 500 °C, concurrently with GC analysis of reactants and products. Characterization of both fresh and used catalysts was performed using AAS, XRD, FESEM-EDX, and *in situ* FTIR techniques to establish a relationship between their structural properties and catalytic performance.

Results and Discussion

The Pd^{2+} ions exchanged into HMOR exhibit an exchange degree of approximately 8%, which is lower than the nominal 23% but significantly higher than that of Pt^{2+}, which is only 1.5%. This indicates a weak interaction between noble-metal cations and the zeolite exchange sites, with Pt^{2+} showing an even weaker interaction than Pd^{2+}. FESEM analysis reveals that the noble-metal particles, roughly spherical, have a maximum diameter of 60 nm for monometallic Pt catalysts and 300 nm for monometallic Pd catalysts. In contrast, bimetallic catalysts exhibit smaller particles, with maximum sizes of 40 nm for Pt,Fe-HMOR and 200 nm for Pd,Fe-HMOR, suggesting that iron species inhibit sintering during thermal treatment.

Unlike Fe-HMOR, the bimetallic Pd,Fe-HMOR and Pt,Fe-HMOR catalysts are effective for the simultaneous reduction of NO and N_2O using CH_4 as the reducing agent in the presence of low O_2 concentration (2500 ppm), at temperatures ≥450°C and ≥400°C respectively, with nearly 100% CO_2 selectivity. N_2O reduction takes place on Fe^{2+} species, which form reactive Fe^{3+}-oxo species. NO_x reduction occurs on Pt or Pd particles with a reduced surface that allows the homolytic cleavage of the N-O bond. The temperature at which this step occurs depends on the CH_4 concentration, as CH_4 must be sufficient to reduce the noble-metal oxide surface. The presence of O_2 in the reaction mixture inhibits the reduction of both N_2O and NO_x by maintaining the noble-metal particles in an oxidized state and promoting the formation of poisoning NO_y species, thereby shifting the light-off of SCRsim at higher temperature. Once O_2 is consumed during combustion, CH_4 reduces the noble-metal oxides, triggering the reduction reactions on the metal sites. At temperatures above the light-off, NH_4^+ species are observed on both bimetallic catalysts, indicating the formation of reactive N, H, C, and O species yielding, besides the main products (N_2, CO_2, CO, and H_2O), NH_3 as by-products (Fig. 1). Ammonia acted as reductant, boosting the reduction of NO_x and N_2O, and in parallel migrates into the zeolite channels, forming NH_4^+ species on Brønsted acid sites.

A comparison between Pt,Fe-HMOR and Pd,Fe-HMOR reveals distinct catalytic activities in SCRsim: Pt,Fe-HMOR shows higher efficiency for NO reduction, while Pd,Fe-HMOR is more effective for N_2O reduction. The superior NO abatement on Pt,Fe-HMOR is likely due to the easier reducibility of Pt species, reflected in a light-off temperature approximately 50 °C lower than that of Pd,Fe-HMOR. The superior N_2O reduction on Pd,Fe-HMOR may be attributed to the presence of Pd^{2+} and Pd^+ species located within the MOR channels. These species form nitrosyls stable up to 500 °C, preventing the formation of poisoning nitrates close to Fe^{2+} active sites. This promotes N_2O reduction on iron active sites. In contrast, PtO_x species in Pt,Fe-HMOR are confined to the external surface.

Overall, the structural characteristics of MOR enable the stabilization of Pt (or Pd) and Fe species, creating a bifunctional catalyst. Noble-metal species on the external MOR surface facilitate NO reduction, while Fe^{2+} species within the channels specifically drive N_2O reduction.

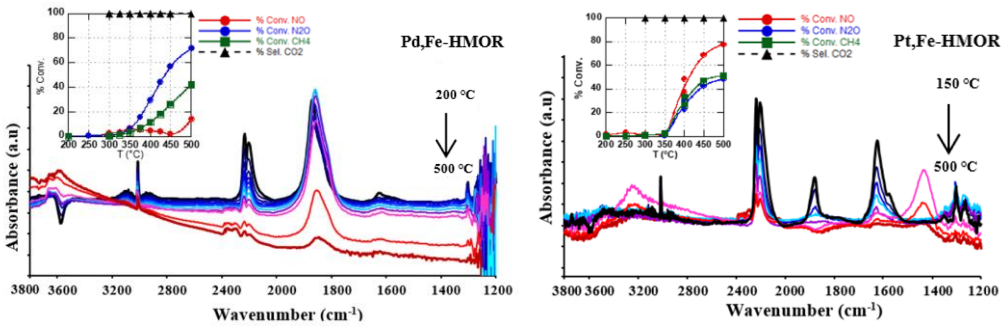


Fig. 1 *Operando* FTIR spectra of surface species during SCRsim at increasing temperature, on catalysts as indicated. In the inset, the reactant conversions *vs.* T are reported. Reactant concentration: $[N_2O]=[NO]=[CH_4]=0.4\%$, $[O_2]=2\%$ (total flow rate=50 cm^3_{STP}/min, He as balance).

References

1. R. Mrad, A. Aissar, R. Cousin, D. Courcot , S. Siffert, *Appl. Catal. A* **2015**, 504, 542-548.
2. https://d2zo35mdb530wx.cloudfront.net/_legacy/UCPthyssenkruppBAIS/assets.files/products___services/fertilizer_plants/nitrate_plants/brochure-envinox_scr.pdf

Acknowledgements

This work was supported by the 'Sapienza' University of Rome (Research Project 2023 - Grant n. RD12318AAD1CD97A).

Descriptors for noble metal redispersion on CeO_2 based catalysts

Florian MAURER[1]*, Agustin SALCEDO[2], Maria CASAPU[1], David LOFFREDA[2], Arik BECK[1], Paolo DOLCET[3], Mimoun AOUINE[4], Thierry EPICIER[4], Stéphane LORIDANT[4], Philippe VERNOUX[4], Carine MICHEL[2], Jan-Dierk GRUNWALDT[1]

[1]*Institute of Chemical Technology and Polymer Chemistry, KIT, Karlsruhe, Germany*
[2]*ENSL, CNRS, Laboratoire de Chimie, Lyon, France*
[3]*Department of Chemical Sciences, University of Padova, Padova 35131, Italy*
[4]*Université Claude Bernard Lyon 1, CNRS, IRCELYON, Villeurbanne, France.*
** florian.maurer@kit.edu*

Significance and Relevance

We tracked the formation of Pt agglomerates and quantified the kinetics of redispersion of individual nano particles using Environmental Electron Transmission Microscopy (ETEM), X-ray Absorption Spectroscopy (XAS), and Density Functional Theoretical (DFT) calculations. By correlating these structural rates to catalytic ones, we were able to identify the redispersion as main descriptor for catalyst deactivation under the given conditions. The observed processes can now be used to develop redispersion-resistant catalysts enhancing the catalytic efficiency of costly and scarce noble metals throughout the lifetime.

Preferred and 2nd choice for the topic: Fundamental advances in understanding catalysis/Air cleaning and combustion
Preferred presentation: Oral preferred

Introduction and Motivations

Predicting the state of catalysts during operation is key for the implementation of reactivation strategies and for the synthesis of long-time stable materials. This is particularly important for catalysts consisting of noble metal particles supported on reducible metal oxides. Such systems based on limited and costly resources are applied in various processes, from fine chemical synthesis to fuel cells and emission control. Recent research has focused on the strong interaction between platinum group metals and CeO_2, which offers unique structural and catalytic properties.[1] While enhancing the low temperature oxidation activity, the strong interaction leads to Pt redispersion under oxidizing conditions at elevated temperatures, which is often accompanied by catalyst deactivation.[2] Conversely, reducing treatments promote the formation of nanoparticles, significantly enhancing the catalytic activity. However, these reactivation strategies are energy-intensive and should be minimized over the catalyst's lifecycle. Therefore, designing redispersion-resistant catalysts at the atomic level while maintaining the active noble metal-CeO_2 interface is crucial.[3] This study investigates the kinetics of Pt redispersion on CeO_2 nanocubes, aiming to quantify it as a function of (1) the local environment, (2) the initial Pt nanoparticle size, and (3) correlating these findings to the integral catalytic activity.

Materials and Methods

With the ultimate aim of following the redispersion with electron microscopy, well-defined CeO_2 nanocubes with a low surface area (23 m^2/g) were chosen as support material as the cubic morphology allows to obtain a parallel alignment of the sample to the electron beam. The nanocubes were loaded with 1.0 wt.% Pt *via* incipient wetness impregnation, maintaining the loading well below an atomic monolayer. XAS revealed that sample treatment in H_2 leads to Pt reduction and formation of nanoparticles with a narrow size distribution of 1-2 nm in diameter. This pre-treatment protocol was replicated in an ETEM using 19 mbar of H_2 at 500 °C. For the redispersion experiment (Fig. 1), oxidizing conditions (500 °C, 1.5 mbar O_2) were applied and the time-dependent decay of individual Pt nanoparticles was observed for few seconds in irregular time intervals over 30 minutes. To minimize possible effects of the electron beam, the beam was blanked in between the measurements. CO oxidation measurements were performed in a lean (10% O_2, 1000 ppm CO) reaction mixture using a

plug-flow reactor. The catalyst activity was monitored during three consecutive light-offs (heating of the catalyst in reaction mixture) before and after a reductive treatment.

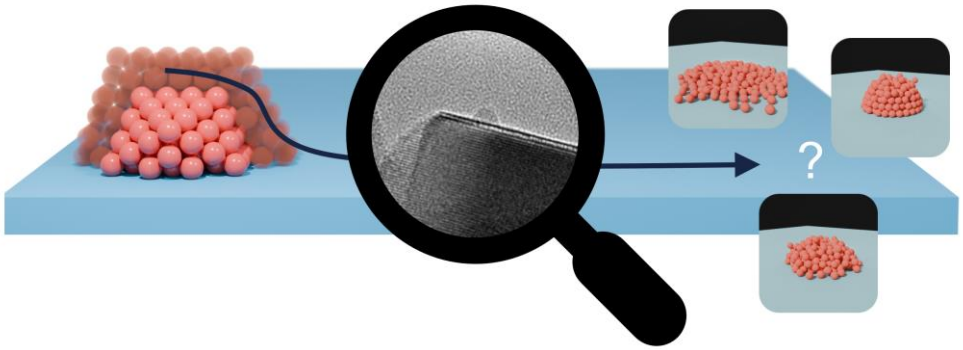


Figure 1 Tracking the redispersion of Pt (red spheres) nanoparticles on a CeO_2 surface (blue) *via* ETEM measurements allows to predict the state under reaction conditions.

Results and Discussion

By following the size and morphology of five Pt nanoparticles during redispersion using ETEM, we were able to correlate the redispersion rate to the local environment of the individual nanoparticles. Hereby it could be shown that redispersion of Pt in the proximity of other nanoparticles is hindered compared to noble metal entities located on the plane CeO_2 surface. Morphological changes during the redispersion process indicate high dynamics, which are also reflected in the interplanar Pt-Pt spacing. Overall, a slight extension of the spacing was observed due to a partial oxidation of the nanoparticles under the conditions used in the microscope.

Based on the redispersion rate, the number of available Pt surface sites was calculated over time assuming a hemispherical shape of the nanoparticle. In closest approximation, the number of exposed surface sites influences directly the reaction rate. By this, a link to the catalytic oxidation activity could be established. The catalytic activity under oxygen rich conditions was monitored using CO as reactant, since the reaction is well-known to be catalyzed only by Pt agglomerates while Pt single perform poorly. As expected, the catalytic activity diminished during the three consecutive light-offs, in line with the noble metal redispersion. Strikingly, the time constant of the loss in activity was in the same order of magnitude as the lifetime of the nanoparticles in the lean mixture. Based on this knowledge, a full prediction of the structural evolution and corresponding catalytic properties of Pt/CeO_2 nanomaterials seems to be possible. This outcome will also help with the rational design of redispersion resistant materials.

References

1. F. Maurer, J. Jelic, J. Wang, A. M. Gänzler, P. Dolcet, C. Wöll, Y. Wang, F. Studt, M. Casapu, J.-D. Grunwaldt, *Nat. Catal.* **2020**, *3* (10), 824–833.
2. A. M. Gänzler, M. Casapu, F. Maurer, H. Störmer, D. Gerthsen, G. Ferré, P. Vernoux, B. Bornmann, R. Frahm, V. Murzin, M. Nachtegaal, M. Votsmeier, J.-D. Grunwaldt, *ACS Catal.* **2018**, *8* (6), 4800–4811.
3. F. Maurer, A. Beck, J. Jelic, W. Wang, S. Mangold, M. Stehle, D. Wang, P. Dolcet, A. M. Gänzler, C. Kübel, F. Studt, M. Casapu, J.-D. Grunwaldt, *ACS Catal.* **2022**, *12 (4)*, 2473-2486.

Acknowledgements

The authors thank the Agence Nationale de la Recherche (ANR) and the Deutsche Forschungsgemeinschaft (DFG) for financial support *via* the DYCAT project (grant No. ANR-19-CE05-0038 and grant No. 431423888, respectively). FM furthermore acknowledges “Fonds der Chemischen Industrie” (FCI) as well as DFG for funding *via* the SFB 1441 TrackAct − Project-ID 426888090.

In-situ DRIFTS studies provide insight into competitive adsorption of VOCs and ozone on catalyst surfaces at low temperature

Amira JABBARI-HICHRI[1], Salma MAJDOUB[1], Eddy J. MORENO[1], Xiaolong JI[1], Valérie MEILLE[1*], Sonia GIL[1*]
[1]*IRCELYON, University of Lyon, CNRS, Lyon, 69626 Villeurbanne Cedex, France*
**valerie.meille@ircelyon.univ-lyon1.fr ; *sonia.gil@ircelyon.univ-lyon1.fr*

Significance and Relevance

This study should lead to improve the understanding of the reaction pathways that take place during O_3 decomposition under realistic operating conditions, *i.e.* under the presence of other air pollutants such as volatile organic compounds (VOCs). Both O_3 and VOCs, that are highly harmful to human health, may be present simultaneously or sequentially in indoor environment such as aircraft cabins. Therefore, to ensure passenger safety and comfort, it is essential to understand the reaction mechanisms involved in the abatement of both indoor air pollutants at the molecular level. This will allow the optimization of a more advanced catalytic converter for aircraft.

Preferred and 2nd choice for the topic: Air cleaning and combustion and Fundamental advances in understanding catalysis
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster): Oral preferred or Short Oral.

Introduction and Motivations

The quality of the air inside an aircraft is a major concern for aviation safety. Indeed, the aircraft cabin environment presents unique challenges, as passengers and crew are exposed to a mixture of compressed jet engine air and recirculated cabin air, resulting in elevated levels of ozone (O_3). Furthermore, ozone is not the only pollutant of concern in aircraft cabins, as the air can also contain other pollutants such as VOCs[1]. These are hydrocarbons that come from kerosene vapors when the aircraft is on the ground, and from engine when the plane is flying even on the ground. The development of catalytic converters to improve cabin air quality and keep pollutants (O_3 and VOCs) levels within acceptable limits is crucial[2]. Furthermore, depending on the altitude, ozone and VOCs may be present simultaneously or sequentially, and although the interaction between them is well understood in the atmosphere, the way in which they compete for adsorption and reaction on the catalyst surface is much less studied. For example, the chemistry at the catalyst surface may depend on the sequence of introduction of different gaseous compounds that can adsorb and/or react with each other on the catalyst surface or the reaction temperature[3]. Therefore, relying on a rigorous *in-situ* Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFTS) approach, our study aims to identify the key intermediates and the reaction pathway involved in adsorption/decomposition of O_3 and/or VOCs.

Materials and Methods

Three materials, 1%Pt/1%Pd-2%Mn/γ-Al_2O_3, 2%Mn/Al_2O_3 and -Al_2O_3, were synthesized using a sol-gel method and characterized by different techniques to assess their physicochemical, textural, surface and acidic properties. Methods employed included N_2 sorption, X-ray diffraction, X-ray photoelectron spectroscopy, H_2 temperature-programmed reduction, pyridine infrared spectroscopy. As it was previously mentioned, the adsorption and catalytic decomposition of both toluene (as a model VOCs) and O_3 on the catalyst surface was evaluated by *in-situ* DRIFTS. The ozone generator was configured to produce 500 ppm ozone in a synthetic air stream at 50 ml/min. A saturator was used to set the concentration of VOCs (70 ppm of toluene) and a mass flow controller (Brooks) for synthetic air. The toluene-air and/or ozone-air mixtures were introduced into the DRIFTS chamber according to the pollutant sequences studied. Various pollutant injection sequences have been applied, for example, at 40°C: surface saturation with toluene (70 ppm-air) for 219 minutes followed by flow of O_3 (500 ppm-air) or a mixture of toluene/O_3 (70 ppm/500 ppm) for 30 minutes. The surface saturation with O_3 (500 ppm-air) for 219 min followed by a mixture of toluene/O_3 (70 ppm/500 ppm) for 30 minutes. The reaction temperature effect (40-120°C) was also investigated.

Results and Discussion

DRIFTS spectra (Figure 1 a) depict the adsorption/oxidation of toluene on the surface of 1%Pt/1%Pd-2%Mn/γ-Al_2O_3 catalyst at 40 °C prior to the ozone exposition for 30 min. These *in-situ* measurements evidenced the formation of peroxides (970-990 cm^{-1}) on the catalyst surface[4,5], which appear to contribute to the formation of partially oxidized surface by-products by accelerating the catalytic removal of toluene, comparing to the conventional catalytic oxidation (not shown). Indeed, the catalytic oxidation of toluene in air atmosphere was only clearly observed at 120 °C, while the ozonation of toluene was observed at 40 °C. The formation of benzyl alcohol, benzoates, benzaldehyde and maleic anhydride species was observed in both cases. Nevertheless, new species such as ketone (benzoquinone), phenyl C-H aromatic and peroxides were observed after O_3 exposition (Figure 1 a)[4-6], suggesting the formation of reactive oxygen radicals (O^{2-}, O_2^{2-}, O^-)[4,5] from the O_3 decomposition, which changes the reaction pathway. Due to the strong oxidation ability of these radicals, toluene can be further oxidized at room temperature. Surprisingly, the bands associated to previous-mentioned peroxides species and the consequently oxidized surface by-products were not observed when the surface catalyst was exposed to a mixture of toluene and ozone after the catalyst saturation with toluene for 219 minutes (Figure 1 b). These results suggest that the prior toluene adsorption potentially obstructs the active sites in this case[7]. This effect was not observed when O_3 was adsorbed prior to exposure to a mixture of toluene and ozone (not shown). However, the formation of peroxides species and new oxidized surface by-products was only clearly observed after 20 min of toluene/O_3 mixture exposition, which also suggests an inhibition effect. Indeed, the catalyst surface seems to be "poisoned" by O_3 at the beginning of the toluene ozonation reaction. Overall, these surface measurements indicate that the reaction pathway is highly dependent on the presence of ozone and on the simultaneous presence or absence of both ozone and toluene. However, further studies are needed to better understand the different observed reaction pathways.

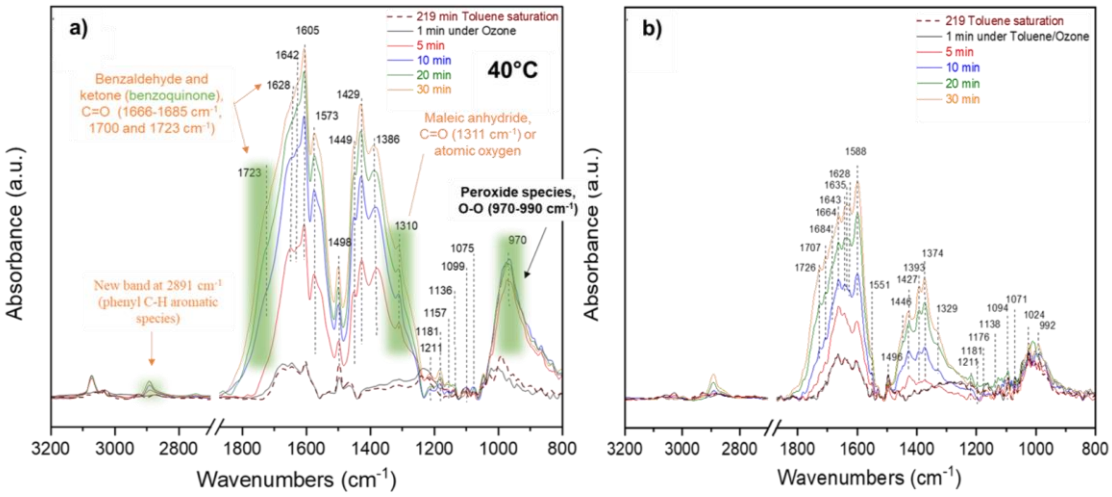


Figure 1. Spectra of **a)** toluene adsorption (dash line) followed by O_3 exposition (solid lines) and **b)** toluene adsorption (dash line) followed by the simultaneous exposition of a mixture of toluene and O_3 (solid lines), all at 40°C.

References

1. M. Masiol et al., *Atmos. Environ*. **2014**, 95, 409.
2. Y. Swesi et al., *Ind. Eng. Chem. Res.* **2021**, 60, 16739.
3. X. Ji et al., *Catalysts.* **2022**, 12, 738.
4. B. Zhang et al., *Appl. Catal. B* 315 (2022) 121552.
5. J. Li et al., Applied Surface Science 311 (2014) 690.
6. J. Houska et al. Environ. Sci. Technol. 57 (2023) 18950.
7. P. Wang et al., *J. Colloid Interface Sci*. **2021**. https://doi.org/10.1016/j.jcis.2021.10.077.

Acknowledgements

The authors gratefully acknowledge the financial partial contribution from BPI France in the framework of the PSPC Régions project "QUALITY AIR".

Anisotropic POCS: Unlocking Mass Transfer Potential

Roberta CASTIGLIONE[1], Claudio FERRONI[1], Federico Sascha FRANCHI[1], Matteo AMBROSETTI[1], Mauro BRACCONI[1], Gianpiero GROPPI[1], Matteo MAESTRI[1], Enrico Tronconi[*,1]
[1]*Laboratory of Catalysis and Catalytic Processes, Politecnico di Milano, 20156 Milan, Italy*
**enrico.tronconi@polimi.it*

Significance and Relevance

The study demonstrates that modifying the POCS diamond lattice geometry by decreasing the strut angle enhances the trade-off between gas-solid mass transfer and pressure drop, achieving up to a two-fold improvement. This topological modification, developed through detailed CFD investigations, enables superior performance over conventional POCS substrates overcoming honeycomb monoliths as well even in terms of pressure drops. Validation through dedicated experiments further highlights their potential for process intensification, offering a novel degree of freedom to design intensified catalytic reactors based on advanced POCS designs.

Preferred and 2nd choice for the topic: Automotive and stationary emission control/ Fundamental advances in understanding catalysis

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Periodic Open Cellular Structures (POCS) are gaining considerable interest as advanced structured materials for process intensification of catalytic reactors[1]. Ceramic-based POCS are particularly attractive for environmental applications, such as exhaust after treatment, due to their ability to optimize the trade-off between mass transfer and pressure drop. In these applications, they present a promising alternative to conventional honeycomb monolith supports. POCS consist of regularly arranged unit cells with interconnected struts forming open windows, creating a permeable 3D structure suitable for fluid flow in all directions. Previous studies identified the diamond lattice as the most promising structure for maximizing the trade off between gas-solid mass transfer and pressure drop. Moreover, motivated by the potential of additive manufacturing to produce customizable lattice materials, in previous works, we have further modified the cell topology[2] by adjusting the angle between the struts and the fluid flow, resulting in a novel geometry with anisotropic permeability in both streamwise and transverse directions[2]. To validate the CFD-derived correlations[2], different POCS were 3D-printed, washcoated and catalytically activated to perform external mass transfer tests under rich H_2 oxidation[3].

Materials and Methods

In a previous work[2], a comprehensive investigation of gas-solid mass transfer and pressure drop, in terms of Merit Index (MI)[4] (Eq.1), in the modified diamond lattice was carried out through detailed CFD simulations. The analysis showed an improvement of MI by decreasing the angle between the struts' axis and the streamwise direction (α), thus obtaining a stretched unit cell along the streamwise direction and shrunken in the transverse directions. An experimental study on the external mass transfer properties was conducted on 4 different POCS characterized by the same porosity ε, same strut diameter d_s, but different angles α. The samples were realised using a lab scale SLA 3D printer and each sample was washcoated with Pt/CeO_2. The probe reaction adopted was the rich-H_2 oxidation[3] (4% H_2, 1% O_2, 95% N_2 v/v) since it is active enough to be operated under mass transfer controlled conditions at temperatures below the resin HDT and the outlet composition of the gas mixture was analyzed with a GC (Agilent HP 6890).

$$MI = \frac{-\ln(1-\chi_{O_2})}{\frac{\Delta p}{\rho u^2}} = \frac{d_s \cdot S_v \cdot Sh_{d_s}}{\phi_{d_s} \cdot Re_{d_s} \cdot Sc} \qquad \text{Where } \phi_{d_s} = \frac{\Delta p}{L}\frac{d_s}{\rho u^2} \qquad \text{(Eq.1)}$$

A 1D PFR mass transfer model has been adopted to interpret the experiments aiming at deriving dimensionless mass transfer coefficients. Due to the high dilution of the system and the isothermal condition verified experimentally, it is possible to adopt the hypothesis of constant volumetric flowrate and constant diffusivity through the length of the reactor. In this way, it is possible to correlate the experimental O_2 conversion with the average Sh number of the system ($Sh_{avg,ds}$):

$$u\frac{d\chi_{O_2}}{dz} = k_{m,O_2}\cdot S_v\cdot\ (1-\chi_{O_2}) \quad \longrightarrow \quad Sh_{avg,d_s} = \frac{-ln\ (1-\chi_{O_2})\cdot u\cdot d_s}{L\cdot \mathcal{D}_{O_2,mix}\cdot S_v} \qquad \text{(Eq.2)}$$

Results and Discussion

To validate the experimental procedure, a catalytic bundle of four monoliths with a circular channel geometry was used. This allowed to compare the Sh number obtained experimentally with the well-known theoretical one of circular ducts. Due to the presence of entry effects (Gz>2), the comparison was made using the Tronconi-Forzatti correlation[5] which accounts them. The tests were performed at flowrates between 10 and 15 NL/min. The experimental conversions were used to evaluate the Sh_{exp} number of the system, and they were compared with the ones obtained from the Tronconi-Forzatti correlation[5] demonstrating a good agreement (Fig. 1a) and validating our experimental methodology.

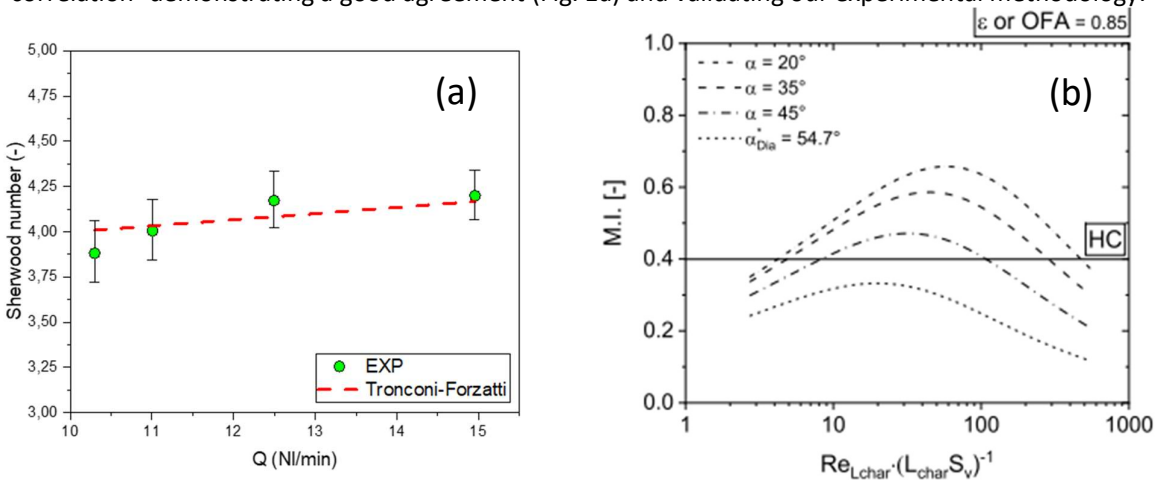


Figure 1: (a) Sh_{exp} (•) and Sh_{avg} T-F(---) VS operative flowrate for monolith bundle with circular channel geometry, (b) Merit Index of the modified diamond lattice as a function of α at constant porosity ε = 0.85

The same procedure has been applied to the evaluation of the external mass transfer properties of the modified diamond lattice. Fig. 1b compares the overall performance of the modified diamond lattice with that of the honeycomb monolith as a function of the Reynolds number. The modified diamond lattice offers up to twice mass transfer coefficients of honeycomb structures at the same pressure drop, demonstrating its strong potential as an enhanced structured substrates for process intensification.

References

1. A. Inayat, J. Schwerdtfeger et al., *Chem. Eng. Sci.* **2011**, 66, 2758–2763
2. C. Ferroni, M. Bracconi et al., *Chem. Eng. & Proc.* **2024**, 195, 109613
3. F.S. Franchi et al., *Cat. Tod.* **2022**, 383, 123-132
4. L. Giani, G. Groppi et al., *Ind. Eng. Chem. Res.* **2005**, 44, 4993–5002
5. E. Tronconi, P. Forzatti, *AIChE* **1992**, 38, 201-210

Acknowledgements

The research leading to these results has received funding from MIUR, FARE RICERCA IN ITALIA, project BEATRICS Grant R16R7NLWPW.

H_2O-assisted Oxidation Half-Cycle of Low Temperature NH_3-SCR over Cu-CHA

Gabriele Contaldo[1], Isabella Nova[1], Matteo Maestri[1,*] and Enrico Tronconi[1,*]
[1]*Politecnico di Milano, Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Via la Masa 34, Milano 20156, Italy.*
**matteo.maestri@polimi.it* **enrico.tronconi@polimi.it*

Significance and Relevance

The detailed mechanistic investigation of the role of H_2O in the oxidation half-cycle (OHC) of NH_3-SCR is here exploited with DFT calculations. We show that H_2O preferentially dissociates over dimeric Cu(I) species to form H_2O_2, a strong oxidant that completes the oxidation of a second pair of Cu(I) moieties in adjacent CHA cages. Such results describe the reaction mechanism of OHC under wet conditions and clarify the active role of H_2O involved in the kinetically-relevant step of the reaction. These interpretations are therefore fundamental in describing at an atomistic level the catalytic phenomena occurring in the redox chemistry of NH_3-SCR.

Preferred and 2nd choice for the topic: Automotive and stationary emission control, Fundamental Advances in understanding Catalysis
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Copper-exchanged chabazite (CHA) zeolites are the state-of-the-art catalysts for the abatement of nitrogen oxides (NO_x) in vehicles exhausts via selective catalytic reduction (SCR) of NO by NH_3[1]. In particular, the detailed reaction chemistry that regulates the Low-Temperature (LT) Standard SCR mechanism has attracted extensive research interest in the last years**,** specifically targeting the relevant role of water in the overall redox chemistry[2]. The scientific community agrees on the redox nature of the global SCR reaction $4\ \ _3 + 4\ \ + \ _2 \rightarrow 4\ \ _2 + 6\ \ _2$, consisting in a reduction half cycle (RHC), where Cu active sites change their oxidation state from Cu(II) to Cu(I), and the subsequent oxidation half cycle (OHC), where Cu(I) is reoxidized. For the RHC, there is converging evidence that Cu(II) is reduced by NO and NH_3 to form linear Cu(I)$(NH_3)_2$ complexes, which are weakly bound to the zeolite and able to diffuse in adjacent CHA cages. On the other side, a detailed Cu-oxidation pathway is unclear, and additional investigation is required to describe a kinetically consistent oxidation scheme. Experimental evidence combined with theoretical calculations show that the presence of water vapor in the feed stream produce a promoting effect that accelerate the rate of the OHC step[3]. These conclusions also reveal that OHC proceed with a NO-silent mechanism, thus suggesting the sole presence of H_2O and O_2 that take part in the total oxidation of Cu(I) moieties. The aim of this work is to provide a detailed description of the oxidation half cycle mechanism by means of theoretical calculations, in order to demonstrate the active role of H_2O in oxidizing Cu(I) moieties and provide fundamental insights of the elementary steps involved in the oxidation emicycle. These results will assess the OHC catalytic cycle under wet conditions at a molecular level, thus paving the way towards a complete understanding of the redox chemistry involved in the NH_3-selective catalytic reduction of NOx.

Materials and Methods

A hexagonal, 36T-sites unit cell is adopted to describe the crystal structure of Cu-CHA. Density Functional Theory (DFT) calculations that include dispersive forces (Grimme D_3) are performed within the generalized gradient approximation (GGA-PBE) functional for the electron exchange and correlation, plane-wave basis-set and norm-conserving pseudopotentials. Brillouin zone samplings are restricted to the Γ-point. All the transition states structures are identified using the climbing-image nudge elastic band methodology (CI-NEB) and vibrational frequency calculations were performed by using a finite-difference approximation of the Hessian matrix implemented in Atomic Simulation Environment (ASE). Molecules in gas phase are assumed ideal.

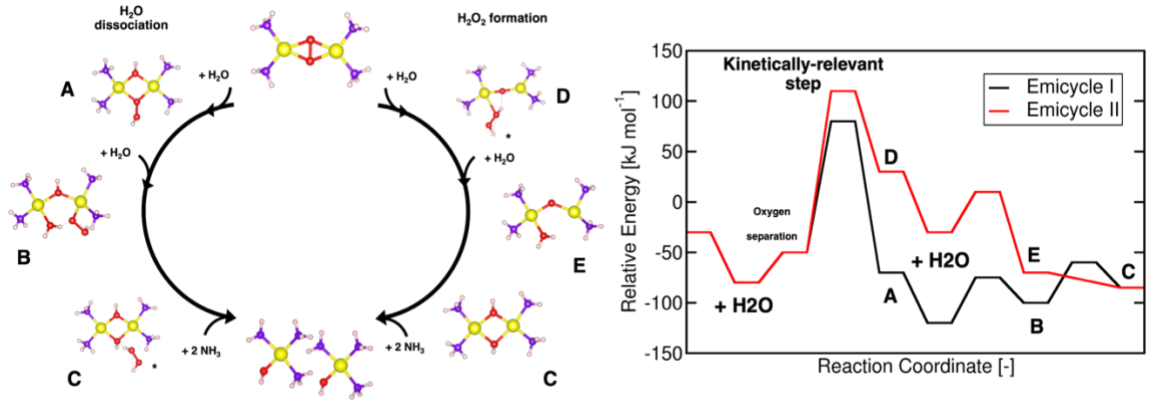


Figure 1: a) H2O dissociation and H2O2 formation mechanisms. b) Minimum Energy Path of OHC.

Results and Discussion

The oxidation half-cycle of NH_3-SCR is studied under wet conditions by adding physisorbed, mobile H2O species in the cage of Cu-CHA. The zero-energy level adopted for the construction of the catalytic cycles corresponds to two $Cu(NH_3)_2$+ complexes within the same cage of CHA and reactants in gas phase conditions. According to our result, O_2 chemisorption on the Cu(I) dimers is exergonic by – 30 kJ/mol, in accordance with available literature[4]. Based on the analysis of the potential energy paths, we find two parallel oxidation cycles, which shares the O_2 activation, i.e. i) the H_2O-dissociation mechanism into OH- and H+ and ii) the direct H2O2 formation pathway, shown in Fig.1 (a). Considering the H_2O-dissociation mechanism, black curve in Fig.1 (b), H_2O dissociates over Cu moieties to form a reacting intermediate (species A) where OH- and H+ ions breaks the oxygen bridge between the Cu moieties with a large electronic barrier of 150 kJ/mol. Then, a second H_2O molecule chemisorbs over one of the two available Cu forming structure B. The energy diagram shows that H+ transfer from the chemisorbed H_2O to form H_2O_2 and structure C has an intrinsic energetic barrier of 40 kJ/mol.

The second mechanism studied consists in the direct H_2O_2 formation over Cu moieties by breaking the oxygen bridge between the two copper moieties (structure D), red curve in Fig.1 (b). The energetic barrier for this step is found to be 200 kJ/mol, larger than the previous mechanism. Moreover, this step is energetically endergonic, with a reaction energy of +90 kJ/mol, resulting in a much unstable structure. Once H_2O_2 detaches from the Cu moiety, a second H_2O molecule chemisorbs (structure E), a H+ is transferred to the second free oxygen atom with an electronic barrier of 50 kJ/mol, finally forming structure C, which is shared between the two proposed mechanisms. The formed H_2O_2 molecule, which is a strong oxidant species, diffuses in an adjacent CHA cage and activates an additional pair of $Cu(NH_3)_2$+ moieties with an energy barrier of 55 kJ/mol. Our results reveal that the H_2O dissociation mechanism is energetically more favorable than the H_2O_2 formation pathway. Moreover, the apparent activation energy obtained for the H_2O-dissociation path is equal to 82 kJ/mol, in excellent agreement with experimental measurements (71-79 kJ/mol[3]). With this study we highlight the relevant contribution of H_2O in the kinetically-relevant step of OHC, elucidating the fundamental insights into the mechanism of the Cu oxidation of NH_3-SCR. These results thus pave the way towards additional computational study of the complex catalytic phenomena involved in NH_3-SCR at atomistic levels of detail.

References

1. C. Paolucci, et Al., Acc. Chem. Res. 2020, 53, 9, 1881-1892
2. G. Contaldo, et Al., ChemCatChem 2023, 15 (20), e202300673
3. N. D. Nasello, et Al., ACS Catalysis 2024, 14, 4265-4276
4. L. Chen, et Al., ACS Catalysis 2020, 10, 5646-5656

Influence of CeO_2 morphology and initial Pd-Pt interaction degree on catalyst activity and stability

Andrea DE GIACINTO[1,2], Paolo DOLCET[1,2], Di WANG[3,4], Joachim CZECHOWSKY[1], Carina MALIAKKAL[3], Christian KÜBEL[3,4], Silke BEHRENS[5], Jan-Dierk GRUNWALDT[1,5], Silvia GROSS[1,2,*], Maria CASAPU[1,*]

[1] *Karlsruhe Institute of Technology, Institute for Chemical Technology and Polymer Chemistry, Engesserstraße 18-20, 76131 Karlsruhe, Germany*

[2] *Università degli Studi di Padova, Dipartimento di Scienze Chimiche, Via Marzolo 1, 35131 Padova, Italy*

[3] *Karlsruhe Institute of Technology, Institute of Nanotechnology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*

[4] *Karlsruhe Institute of Technology, Karlsruhe Nano Micro Facility, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*

[5] *Karlsruhe Institute of Technology, Institute of Catalysis Research and Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*

** e-mail corresponding: maria.casapu@kit.edu; silvia.gross@unipd.it*

Significance and Relevance

The impact of the support morphology and Pd-Pt interaction degree was systematically investigated during CO oxidation. Constant surface noble metal concentration (SNMC) ensured the same probability for noble metal (NM) aggregation/redispersion under reaction conditions on commercial CeO_2, nanocubes and nanorods. E*x situ* and *in situ*/*operando* characterization tools revealed that the aggregation/redispersion of the NM is controlled by the morphology of ceria. On CeO_2-nanocubes a balanced NM-support interaction is obtained that promotes the formation of small and active clusters. In contrast, a high number of surface defects, as present for CeO_2-nanorods, foster the formation of highly dispersed and less active species.

Preferred and 2nd choice for the topic: *1) Automotive and stationary emission control, 2) Fundamental advances in understanding catalysis*

Preferred presentation: Oral preferred or short oral

Introduction and Motivations

Exploiting the interaction between the noble metals and reducible metal oxide supports has attracted a tremendous interest during recent decades for various catalytic applications including emission control[1,2], fine chemistry, electrocatalysis and energy-related processes[3]. Previous studies have shown that the activity, selectivity and stability of CeO_2-based catalysts is influenced by the porosity, reducibility and morphology/exposed facets of the support as well as by the interplay with the NM nanoparticles (NPs)[4,5]. On the latter aspect, we have recently shown for monometallic catalysts that the surface noble metal concentration (SNMC) influences the *in situ* formation of the active species and the onset of oxidation reactions[6,7]. As a next step, this study focuses on understanding the effect of Pd-Pt alloying extent and CeO_2 morphology by comparing bimetallic catalysts with the same SNMC supported on hydrothermally synthesized and morphologically pure CeO_2-nanocubes and nanorods. A commercial ceria support was used as a reference system for non-preferential exposed facets.

Materials and Methods

Different CeO_2 morphologies were obtained by hydrothermal synthesis. Bimetallic and alloyed Pd-Pt NPs were prepared by colloidal synthesis, and were afterwards deposited on the ceria supports via wet impregnation. To modify the Pd-Pt alloying degree, the noble metal precursors were varied during the synthesis process. The effect of the ceria morphology was highlighted by maintaining the same SNMC in all samples. The NM structural dynamics and the interactions between Pd, Pt and CeO_2 were then

monitored by complementary characterization methods after synthesis, during catalyst pretreatment and under reaction conditions.

Results and Discussion

Ex-situ characterization of the bare CeO_2 supports revealed different exposed facets and oxygen vacancies concentrations depending on the ceria morphology. At the same time, alloyed nanoparticles or highly dispersed Pd-Pt species were identified for the differently prepared bimetallic catalysts. Accordingly, pronounced differences were measured in the CO oxidation activity and catalyst stability depending on the exposed facets of the CeO_2 support and noble metal state. In line with these results, *operando* XAS data obtained during consecutive light-off/light-out cycles and pre-treatment procedures indicate a higher structural stability for the alloyed Pd-Pt nanoparticles on CeO_2-nanocubes.

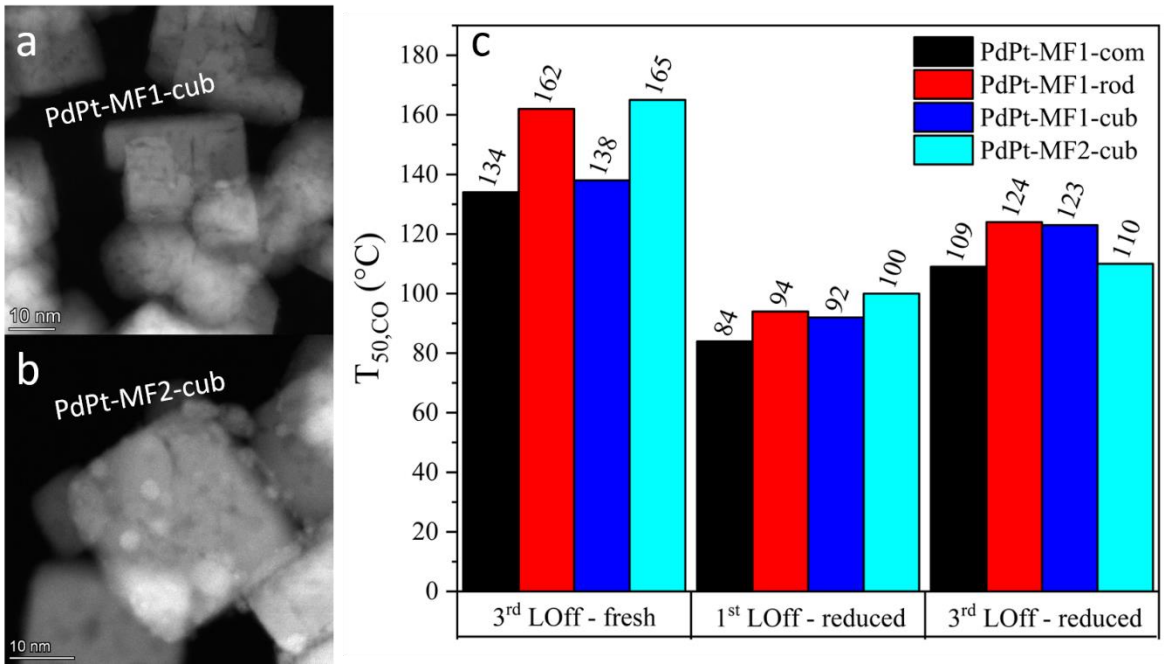


Figure 1: HAADF-STEM images of highly dispersed (a) and alloyed (b) Pd-Pt bimetallic catalysts after catalytic tests. (c) Temperatures of 50% CO conversion at different stages of the catalytic test for the investigated samples.

Acknowledgements

This study was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – SFB 1441 – Project-ID 426888090 (projects B2, C2). S.G. gratefully acknowledges DFG for provision of a Mercator Fellowship.

References

1. Datye, A. K.; Votsmeier, M. *Nat. Mater.* **2021**, *20* (8), 1049–1059.
2. Lee, J. E.; Ok, Y. S.; Tsang, D. C. W.; Song, J. H.; Jung, S. C.; Park, Y. K, *Sci. Total Environ.* **2020**, *719*, 137405.
3. Ding, S.; Hülsey, M. J.; Pérez-Ramírez, J.; Yan, N., *Joule* **2019**, *3* (12), 2897–2929.
4. Gänzler, A. M.; Casapu, M.; Vernoux, P.; Loridant, S.; Cadete Santos Aires, F. J.; Epicier, T.; Betz, B.; Hoyer, R.; Grunwaldt, J. D., *Angew. Chemie - Int. Ed.* **2017**, *56* (42), 13078–13082.
5. Casapu, M.; Fischer, A.; Gänzler, A. M.; Popescu, R.; Crone, M.; Gerthsen, D.; Türk, M.; Grunwaldt, J. D., *ACS Catal.* **2017**, *7* (1), 343–355.
6. Maurer, F.; Beck, A.; Jelic, J.; Wang, W.; Mangold, S.; Stehle, M.; Wang, D.; Dolcet, P.; Gänzler, A. M.; Kübel, C.; Studt, F.; Casapu, M.; Grunwaldt, J. D., *ACS Catal.* **2022**, *12* (4), 2473–2486.
7. Gashnikova, D.; Maurer, F.; Sauter, E.; Bernart, S.; Jelic, J.; Dolcet, P.; Maliakkal, C. B.; Wang, Y.; Wöll, C.; Studt, F.; Kübel, C.; Casapu, M.; Grunwaldt, J. D., *Angew. Chemie - Int. Ed.* **2024**, *63* (35).

Functionalization of hydroxyapatite with silver for application in total oxidation of formaldehyde

E. Prandini[1,2], G. Abdallah[1], S. Campisi[2], A. Gervasini[2], A. Addad[3],
O. Gardoll[1], M. Trentesaux[1], J.-M. Giraudon[1*], J.-F. Lamonier[1]

[1] *Univ. Lille, CNRS, Centrale Lille, Univ. Artois, Unité de Catalyse et Chimie du Solide-Lille, 59000, France.*
[2] *Dipartimento di Chimica, Università degli Studi di Milano, Via C. Golgi 19, Milano, 20133, Italy.*
[3] *Univ. Lille, CNRS, INRAE, Centrale Lille, Unité de Matériaux et Transformations-Lille, 59000, France*

** jean-marc.giraudon@univ-lille.fr*

Significance and Relevance

New "in flow" and conventional "batch" methods (IFM and BM) were used for the preparation of Ag-modified hydroxyapatite (Ag-HAP) catalysts. HAP supported Ag_3PO_4 NPs were synthesized by BM while most part of silver appears as highly dispersed Ag species on HAP when using IFM. The best intrinsic activity for HCHO oxidation into CO_2 in moist air (RH=50%) was achieved over Ag-HAP prepared by IFM and subsequently calcined at 500°C. The highly dispersed Ag NPs and the presence of water likely promote HCHO oxidation through a hydroxide-active oxygen pathway. This work offers valuable insight for design of new efficient Ag-HAP catalysts.

Preferred and 2nd choice for the topic: Air cleaning and combustion, Automotive and stationary emission control
Preferred presentation: Oral preferred

Introduction and Motivations

Formaldehyde (HCHO) is an irritant and carcinogenic volatile organic compound (VOC) released primarily by the degassing of wood-based panels which may cause serious health hazards. Much effort has been devoted to eliminate HCHO, with catalytic oxidation being one of the most effective methods.

Noble metal-based catalysts such as Pt and Au exhibit high activities on formaldehyde oxidation. However, due to the high cost of precious metals, developing low-cost catalysts remains a significant challenge. Among the various alternatives, Ag-based catalysts are much cheaper and show considerable efficiency for HCHO oxidation at low temperature[1].

The aim of this work is to study the catalytic performances of new silver-functionalized calcined hydroxyapatite (HAP, $Ca_{10}(OH)_2(PO_4)_6$) for the total oxidation of formaldehyde in dry/wet air. HAP, the most abundant CaP mineral, can serve as a catalytic support thanks to its high specific surface area, versatile ion-exchange property and surface area exposed to OH^-, PO_4^{3-}, and Ca^{2+} entities[2]. Functionalization of as-synthesized hydroxyapatite with silver was carried out using "batch" and "in-flow" methods, and the effect of subsequent calcination temperature (300°C-500°C) on physical properties and catalytic performances in HCHO oxidation was investigated.

Materials and Methods

IFM: A flowing $AgNO_3$ aqueous solution (100 mL- 1.3 mL/min) was allowed to pass through the compact bed of HAP. The solid F-Ag/HAP was obtained after a vacuum treatment and drying.

BM: An aqueous solution of $AgNO_3$ (250 mL) was added to HAP (~6 g). The reaction mixture was stirred for 24 h at 40°C. The suspension was filtered, washed and dried (120°C-16 h) to get B-Ag/HAP. The Ag content was calculated to obtain a nominal Ag loading of 3 % w/w in both cases.

The as-prepared samples (≈ 500 mg) were calcined at 300 °C and 500 °C (2°C/min) in dry flowing air (0.2 L/min) to get the B-Ag/HAP-T F-Ag/HAP-T samples (where T stands for the temperature in °C).

Catalytic tests were performed with 200 mg of catalyst (100 < particle size < 200 µm) loaded in a glass tubular micro-reactor (inner diameter: 10 mm). The powders were activated 1 h at 100 °C in a

dry air flow (100 mL/min) before being submitted to 100 ppmv HCHO/synthetic air for 4 h (GHSV: 30 L /(g.h).

Results and Discussion

Silver content for B-Ag/Hap and F-Ag/Hap of 1.9 and 0.8 wt% differs from a factor 2 in line with the IFM ensuring a minimization of the contact time between Ag and HAP. XRD results show that HAP supported Ag_3PO_4 NPs with a crystalline structure were synthesized by BM while most part of silver appears as highly dispersed Ag(I) species on HAP with a minor contribution of $Ag_3(PO_4)$ when using IFM. The calcination step at 300°C shows persistence of the diffraction peaks relative to the cubic $Ag_3(PO_4)$ phase for B-Ag/HAP while it is noted the quasi-absence of Ag related phase for F-Ag/HAP. After calcination at 500°C it is only observed the peaks characteristic of HAP which implies the high dispersion of Ag species on HAP on both samples. However, the H_2/Ag ratios determined from the H_2-TPR experiments are below 0.5 for B-Ag/HAP-500 suggesting that Ag(I) species are not completely reduced to Ag(0). By opposition, the absence of H_2 consumption peaks indicates the full conversion of Ag(I) species into Ag(0) NPs in the preparation step, as shown in Fig. 1a for F-Ag/HAP-500, which are recognized to activate O_2. The textural properties analysed from nitrogen sorption isotherms show minimal differences among the different series of catalysts as compared to those of the HAP support. Interestingly, XPS atomic ratios Ag/Ca and Ag/P (with Ag 3d corrected from the Ca 2p energy loss) indicate a better Ag dispersion for the catalysts of the IFM series. The CO_2 yield (Y_{CO2}) for HCHO total oxidation at 100°C in dry (non-calcined catalysts) and moist air (RH = 50%) for 4 h on time-on-stream (TOS) are given in Fig. 1b, showing the beneficial role of a calcination step at 500°C on the conversion of HCHO into CO_2 while calcination at 300°C leads to low efficient catalysts.

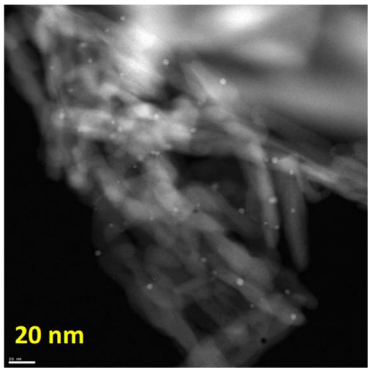


Fig. 1a : STEM-HAADF image of F-Ag/HAP-500

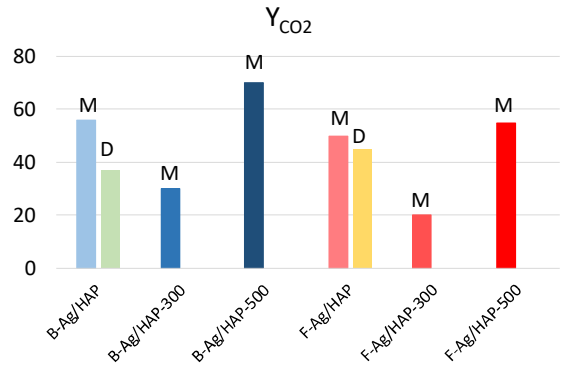


Fig. 1b : Y_{CO2} (%) for HCHO total oxidation over catalysts at 100°C after a TOS of 4h in dry (D) and moist (M) air.

The results showed that the mode of preparation affects the Ag content and the nature/distribution of silver species. The highly dispersed Ag(0) nanoparticles on IFM samples, combined with the presence of water, likely enhance HCHO oxidation via a hydroxide-active oxygen pathway. This mechanism results in superior catalytic activity, also considering the lower Ag concentration compared to BM samples.

References

1. R. Fang, M. He, H. Huang, Q. Feng, J. Ji, Y. Zhan, Dennis Y.C. Leung, W. Zhao, *Chemosphere,* **2018**, *213*, 235.
2. M. Ibrahim, M. Labaki, J.-M. Giraudon, J.-F. Lamonier, *Journal of Hazardous Materials*, **2020**, 383, 121139.

Acknowledgements

The authors thank Laurence Burylo and Pardis Simon for their contribution in XRD and XPS measurements, respectively.

LOHC: kinetics of toluene hydrogenation over Pt/Al_2O_3 catalyst in a trickle bed reactor

Vincenzo RUSSO*[,1], Muhammad Usama DAUD[1], Alessandro ESPOSITO[1], Federica COSENZA[1], Riccardo TESSER[1], Martino DI SERIO[1]

[1] *Università di Napoli 'Federico II', Department of Chemical Sciences, Napoli, Italy*.

* v.russo@unina.it

Significance and Relevance

The main novelty of the paper was the kinetic investigation of toluene hydrogenation to methylcyclohexane using 5wt.% Pt/Al_2O_3 catalyst, packed in a trickle bed reactor. The catalyst shown good activity, stability, and total selectivity to the desired product, representing a good candidate for LOHC technology. Kinetic information was retrieved on the collected data, having hints on the reaction mechanism, showing that the reaction follows an Eley-Rideal model.

Preferred and 2nd choice for the topic: H_2 storage and transportation, green H_2 production, hydrogen vectors, Fundamental advances in understanding catalysis.
Preferred presentation: Oral only

Introduction and Motivations

Hydrogen is considered nowadays a clean energy vector. However, to date, one of the factors delaying its adoption as a fuel is the lack of adequate storage and transport systems. Conventionally, hydrogen storage is done by high-pressure compression or cryogenic liquefaction, but both techniques include safety issues, low storage density, evaporative losses and relatively high costs.

A promising alternative to counteract the problems associated with these techniques is the use of Liquid Organic Hydrogen Carriers (LOHC), which are organic compounds that can store and release hydrogen through a cycle of chemical reactions of hydrogenation and dehydrogenation[1]. These reactions require to be promoted by suitable catalytic systems, usually represented by transition metals (e.g., Ni, Ru, Pd or Pt) fixed in the form of a fine powder on a porous support (e.g., Al_2O_3).

The present work is concerned with studying the continuous hydrogenation reaction of toluene, thus used as a carrier molecule, to give methylcyclohexane, catalysed by platinum supported on alumina (Pt/Al_2O_3). Considering the three-phase gas-liquid-solid system, the reaction was conducted in a trickle bed reactor (TBR) and, by appropriately varying the operating conditions, several tests were carried out to retrieve kinetic information on the chemical reaction. Flow chemistry principles were exploited to increase the performance of the process, with the advantages of better control of reaction conditions, rapid analysis and reduced diffusion limitations.

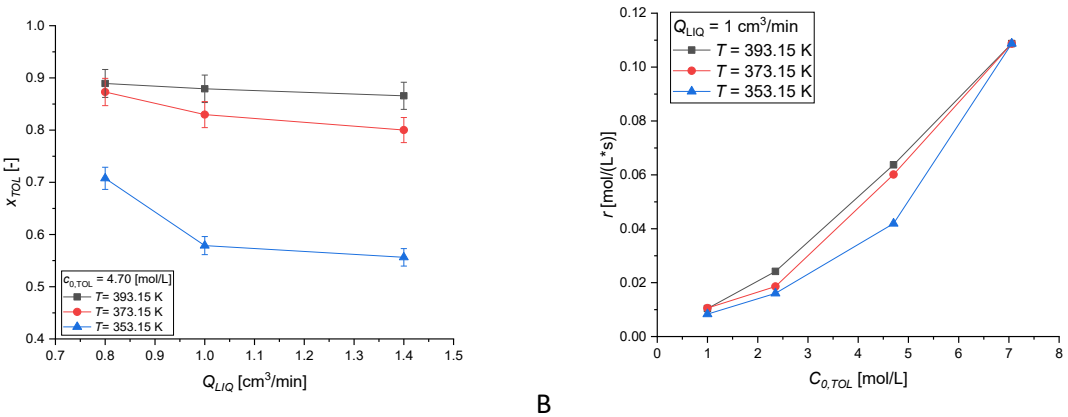
Materials and Methods

In the present study, high-purity toluene (99.5%) and n-heptane (≥99%) were purchased from Merck, along with a commercial catalyst, 5wt.% $Pt\text{-}Al_2O_3$ in powdered form (40µm average radius). Catalyst pre-reduction was conducted in a glass-bed reactor at 130°C under a hydrogen flow rate of 0.05L/min for 3 hours to activate the metallic phase.

Kinetic experiments were conducted in a 10 cm trickle bed reactor with a 0.635 cm inner diameter, loaded with 104.3mg of catalyst (ρ_B=0.02g/cm^3). The reactor was heated up at the desired temperature level with via electrical resistance. Azura P 4.1S HPLC pump was used to pump the liquid solution to the reactor, while two gas flowmeters regulators were adopted to feed nitrogen and hydrogen to the reactor, at a defined volumetric ratio. A gas-liquid separation unit was put in series to the trickle bed reactor, enabling the collection of liquid samples. The liquid phase was analyzed via GC-FID analysis (Perkin Elmer Clarus 500) using Elite 5 column (*ID*=0.32mm *L*=30m, film thickness=0.25µm, composition of the stationary phase: 5% diphenyl/95% dimethylpolysiloxane). Each sample, diluted with heptane, was injected with a 1 µL syringe at 250 °C. The chromatographic run involved an initial step at *T*=90 °C held for two minutes, followed by two temperature ramps: 2 °C/min up to 120 °C (held for one minute) and a rapid increase to 200 °C at 40 °C/min.

Results and Discussion

Figure 1A shows the trend of toluene conversion to methylcyclohexane as a function of the liquid flow rate for the 3 different temperatures, highlighting the influence of temperature and flow rate on the process. An inverse proportionality between the conversion degree and the volumetric flow rate, indicating negligible fluid-solid mass transfer limitations. Moreover, there a strong effect of temperature was measured: passing from 80 to 100 °C there is a significant conversion difference and, in addition, at the highest temperature, diffusion phenomena probably begin to occur, as only a minor influence of the volumetric flowrate was measured. It must be noted that in every experiment selectivity was always 100% towards methylcyclohexane, and the catalyst was stable for 50h of time on stream.



A B

Figure 1 A. Evolution of the toluene steady-state conversion at different liquid flow-rate and at different temperatures, imposing $c_{0,TOL}$=4.7mol/L, Q_G=5cm^3/min and N_2/H_2=4:1vol/vol. B. Evolution of the observed reaction rate as a function of the feed toluene concentration, at different temperatures, imposing Q_L=1cm^3/min, Q_G=5cm^3/min and N_2/H_2=4:1vol/vol.

The hydrogenation reaction rate dependence with the feed toluene concentration was studied at different temperatures (Figure 1B). At each temperature, the reaction rate increases with the concentration of the reactant in the feed, revealing a shift of the reaction order when increasing the temperature. In particular, a first order behavior can be observed at the highest temperature value, while at lower temperatures, the apparent order is lower than one. These peculiar trends could be explained by assuming surface reaction mechanism (e.g., Langmuir-Hinshelwood, Eley-Rideal). In particular, an Eley-Rideal mechanism for the hydrogenation reaction is hypothesized, assuming that hydrogen reacts from the bulk of the liquid phase, at a constant hydrogen concentration, the reaction rate is given as in Eq. 1 in both explicit and simplified form.

$$= \frac{2}{1 + \quad + \quad _2 \quad _2} = \frac{'}{+} \quad (1)$$

As physical adsorption is an exothermic process, it is reasonable to hypothesize that at high temperatures, $K_{TOL}C_{TOL}$<<α, leading to a first order reaction rate, r=k''C_{TOL}. Conversely, at lower temperatures, $K_{TOL}C_{TOL}$>>α, thus the apparent reaction order shifts from 1 to zero. At intermediate temperatures, it is plausible that the apparent order is between 0 and 1.

In conclusion, the present study allowed to retrieve important information on the reaction kinetics, useful for a future scale-up with the related design of dedicated chemical plants.

References

1. M. Niermann, A. Beckendorff, M. Kaltschmitt, K. Bonhoff, *International Journal of Hydrogen Energy* **2019**, *44(13)*, 6631-54.

Green NH_3 Synthesis via Hydroxyapatite-Supported Ru Catalysts for Sustainable H_2 Storage under mild conditions

Sabrina Akrour[1], Alexandre Vimont[2], Sandra Casale[1], Guylène Costentin[1] and Cyril Thomas*[1]
[1]*Sorbonne Université, CNRS, Laboratoire Réactivité de Surface, LRS, Paris, 75005, France*
[2]*Normandie Université, Laboratoire Catalyse et Spectrochimie, 14000 Caen, France*
**e-mail : cyril.thomas@sorbonne-universite.fr*

Significance and Relevance

This research demonstrates the potential of hydroxyapatite (HAp) as a novel support for ruthenium (Ru) nanoparticles, enabling efficient ammonia synthesis under milder conditions (1 bar). By optimizing the basicity of HAp, through controlled Ca/P ratios catalytic performance was enhanced, with the best results showing a 60% improvement in NH_3 turnover frequency (TOF) compared to a benchmark Ru/MgO catalyst. In particular, the study shows that the basicity of HAp plays a critical role in facilitating electronic transfer to Ru NPs, leading to improved nitrogen activation. Such advances are significant for achieving sustainable fertilizer production and clean energy solutions through more efficient ammonia synthesis.

Preferred and 2nd choice for the topic: (1) H_2 storage and transportation, green H_2 production, hydrogen vectors. (2) Sustainable and clean energy production and transport.

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Ammonia (NH_3) plays a dual role as a key fertilizer in global agriculture and as a promising hydrogen (H_2) carrier for renewable energy storage[1]. Traditionally, NH_3 synthesis via the Haber-Bosch process requires severe conditions, high temperatures (400-600 °C) and pressures exceeding 200 bar, accounting for nearly 2% of global energy consumption and producing substantial greenhouse gas emissions[2]. Improving this process to achieve efficient NH_3 production under milder conditions remains a significant challenge. Ru catalysts have been reported to be more active than conventional iron (Fe) and nickel (Ni) catalysts[3] and Ru/MgO has been considered as a benchmark catalyst for NH_3 synthesis[4]. It has been suggested that the basic nature of the support enhances the electron density of Ru, which facilitates the dissociation of the nitrogen triple bond N≡N that is claimed to be the rate-limiting step in NH_3 synthesis.

The present study investigates original hydroxyapatite-supported Ru catalysts for NH_3 synthesis. HAp is an environmentally friendly calcium phosphate known both for its high ability for metal dispersion[5] and for its basic properties that can be tuned by modifying its composition (Ca/P ratio) by adjusting the pH of the precipitation medium[6]. The influence of the synthesis conditions on the basic properties of the HAp supports, on the dispersion and electronic density of the Ru nanoparticles (NPs) are studied and discussed in line with the evolution of the TOF) for NH_3 synthesis.

Materials and Methods

HAp supports were synthesized by adding a phosphorus precursor solution ($NH_4H_2PO_4$) to a $Ca(NO_3)_2$ solution at 80 °C, at stationary pH ranging from 6.5 to 9.0 by controlled addition of NH_4OH and by using an Optimax 1001 workstation (Mettler Toledo). Subsequently, Ru (1-5 wt%) was deposited by wet impregnation of $Ru(NO)(NO_3)_3$ and the metallic nanoparticles were obtained by reduction under H_2 at 450 °C for 2 h. ICP-OES chemical analysis, N_2 sorption, XRD, SEM, TEM and N_2-FTIR were used to characterize Ru/HAps and the catalytic conversion of 2-methylbut-3-yn-2-ol was used as a model reaction to investigate the acid-base properties of HAps. Ammonia synthesis was performed in a fixed-bed flow reactor (FR-100, Micromeritics) with a 50 mL/min H_2:N_2 (3:1) flow at 1 bar using 100 mg of catalyst diluted with 4.8 g of SiC. The NH_3 concentration at the reactor outlet was recorded every 5 seconds using an on-line MKS 2030 infrared analyzer.

Results and Discussion

Properties of the Ru/HAp catalysts: Crystalline (XRD) rod-like (SEM) HAps with a global increase in Ca/P ratio with increasing precipitation pH were successfully prepared. All of them show very similar specific surface areas of about 35 m^2/g. For all of the HAp_pH supports, well-dispersed Ru nanoparticles of 2.1 ± 0.2 nm (TEM) were obtained after reduction. This particle size was maintained with increasing Ru loading.

Catalytic performance: Ru/HAp catalysts were found to be active and stable with time on stream (at least 3 days) for NH_3 synthesis. The catalytic measurements showed that varying the Ru content on HAp had a limited effect on the TOF values for NH_3 production. In contrast, the Ca/P ratio of the HAp support, modulated by the precipitation pH, significantly affected the TOF, reaching an optimum of 0.41 min^{-1} at 400 °C for Ru (2 wt%)/HAp_7.6. This TOF was found to be about 60 % higher than that of a Ru/MgO benchmark catalyst (**Figure 1a**). This finding is consistent with the higher basicity of the corresponding support as measured by the 2-methylbut-3-yn-2-ol model conversion reaction. In addition, N_2 adsorption on Ru^0 NPs at 100 K followed by FTIR showed the most pronounced shift of the maximum of the N_2 absorption band toward lower wavenumbers (2191 cm^{-1}) for Ru (2 wt%)/HAp_7.6 (**Figure 1b**), which is consistent with an increased electron density of the Ru^0 NPs for such a sample.

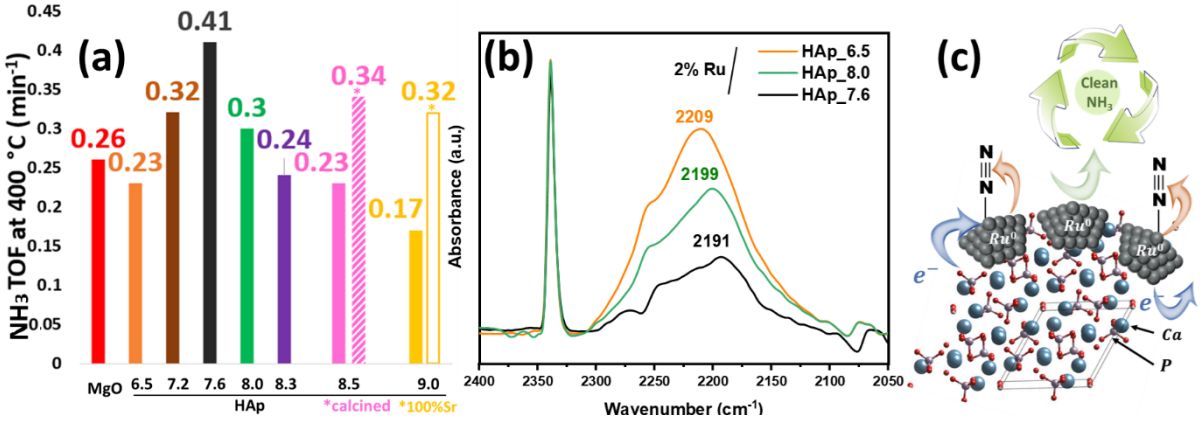


Figure 1. (a) NH_3 TOF at 400 °C and 1 bar over Ru/MgO and Ru/HAp_pH catalysts, (b) N_2-FTIR spectra at 100 K. (c) Schematic representation of the influence of HAp basicity on NH_3 synthesis.

Optimization paths: Better dispersion of the Ru NPs was achieved by performing a calcination step at 600 °C of the HAp support prior to Ru deposition. This reduced the size of the Ru NPs to 1.7 nm and resulted in an increase in TOF of about 50% for the calcined HAp_8.5 support compared to uncalcined HAp_8.5 (**Figure 1a, purple bars**).

Sr bulk-substituted HAp (Sr-HAp) was also prepared by coprecipitation, and the Sr-HAp support was found to be more basic than its Ca counterpart. This resulted in an increase in NH_3 TOF of about 90% for Ru/Sr-HAp_9.0 compared to Ru/HAp_9.0 (**Figure 1a, yellow bars**). These results not only highlight the potential of HAps and modified HAps as supports for Ru in NH_3 synthesis, but also provide a clear proof of concept of the critical role of the basic properties of the support on the electronic density of the Ru particles, and in turn on the activation of N_2 (**Figure 1c**).

References

(1) A. Afif et al., *Renew. Sustain. Energy Rev* **2016**, *60*, 822.
(2) Q.Wang et al., *J. Energy Chem* **2019**, *36*, 25.
(3) H. Fang et al., *ACS Catal* **2022,** *12*, 3938.
(4) X. Ju et al., *ChemCatChem* **2019,** *11*, 4161.
(5) M. Akri et al., *Nat. Commun* **2019,** *10*, 1.
(6) T. Tsuchida et al., *J. Jpn. Petrol. Inst* **2009**, *52*, 51.

Acknowledgements

S. Akrour acknowledges funding from the ANR project H_2CASTORAMA (ANR-22-CE05-0002) and the PhD grant managed by the Centre National de la Recherche Scientifique (CNRS).

Solar Photoreforming of biomass and plastic-derived materials using carbon-based photocatalysts

Maria Teresa ARMELI IAPICHINO[1*], Roberto FIORENZA[1], Salvatore SCIRE'[1]
[1]*University of Catania, Department of Chemical Sciences, V.le Andrea Doria 6, Catania, Italy.*
** maria.armeliiapichino@phd.unict.it*

Significance and Relevance

Energy from renewables is central for the sustainability. Sunlight-driven fuels production is a sustainable and economical approach to generate energy vectors, such as hydrogen, through solar photoreforming. In addition, a today relevant challenge is the management of the countless natural wastes, such as lignocellulose with $120*10^9$ T/y produced from agricultural, grass and wood[1]. Furthermore, the contextual presence of synthetic waste such as plastic materials like PS, PP or PE (production of $800*10^9$ T/y)[1] amplifies this environmental issue. Therefore, the novelty of this work is the use of non-critical photocatalysts, in the solar photoreforming of biomass and plastic-derived materials.

Preferred and 2nd choice for the topic: (1) H_2 storage and transportation, green H_2 production, hydrogen vectors; (2) Photocatalysis and photoelectrocatalytic approaches, solar energy utilization
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Photocatalytic hydrogen production is amongst the top ten emerging technologies in chemistry. In particular, the photoreforming (PR) of organic substrates is an attractive way to obtain green H_2 together with the valorization of waste or biomass. This process combines water reduction with the oxidation of a sacrificial agent using a semiconductor. The choice of the organic substrate is fundamental to promote the H_2 production. In this work, we originally proposed waste-derived materials (biomass and plastics) as organic scavengers in order to produce H_2 with the simultaneous waste disposal. However, one of the necessary steps for the waste photoreforming reaction is the efficient solubilization of these organic substrates through various pre-treatments as the alkaline hydrolysis, using at the same time a photocatalytic system resistant at these extreme conditions. In recent years the scientific community focused on the study of carbon-based materials for their remarkable electrical, thermal and mechanical properties. The focus of this work was to investigate the performance of metal carbides MC (SiC, MoC, TiC) combined with the graphitic carbon nitride (g-C_3N_4) in different amounts. The carbon nitride possesses the advantages of low cost, non-toxic, thermodynamic stability, and remarkable optical properties[2]. The metal carbides show promising applications, with excellent physicochemical properties, such as high adsorption capacity, high melting point, good electrical conductivity, high thermal stability, and hardness[3].

Materials and Methods

For the preparation of bulk g-C_3N_4 a thermal polymerization has been used as reported in ref[2]. The MC systems were prepared with a hydrothermal synthesis[4]. The two materials were joined through a physical treatment by sonication followed by a calcination in an oven. The photocatalytic tests were performed with 50 mg of the photocatalyst, homogeneously suspended in an aqueous solution containing the sacrificial agent (40 mL of deionized water and 10 mL of biomass (cellulose) and plastics (PS, PE)-derived materials, previously pre-treated) inside the reactor. Then, the reactor was irradiated for 5 h using a solar lamp [5]. On the most promising photocatalysts, in order to increase the production of H_2, Pt (1 wt%) has been added as co-catalyst, using the wetness impregnation method.

Results and Discussion

The focus of this work is the study of the performance of carbon-based catalysts as g-C_3N_4 and MoC introducing Pt as co-catalysts to further improve the H_2 formation.

A good production of H_2 was verified with all the investigated sacrificial agents (Fig.1)- Interestingly an increase of H_2 production was found in the presence of carbon nitride and a further increase with the addition of Pt. The PS photoreforming led to the lowest H_2 production. This can be due to the fact that synthetic waste, such as plastic, has C-C bonds that are extremely difficult to break, especially in the presence of an aromatic ring as the PS case. Furthermore, in the case of cellulose, the basic pH pre-treatment allows to improve the electrostatic interaction between the organic substrate and the catalyst. The performance of the MoC-g-C_3N_4 composites, prepared with an easy procedure, was promising to propose a new class of unconventional photocatalysts, instead of the most used metal oxides-based systems. The performance will be compared to similar systems as SiC-g-C_3N_4 and TiC-g-C_3N_4 composites. The results obtained in this work can pave the way for future perspectives in which the wastes or the pollutants can be considered new raw materials to obtain H_2, preserving, at the same time, the environment by the emerging contaminants.

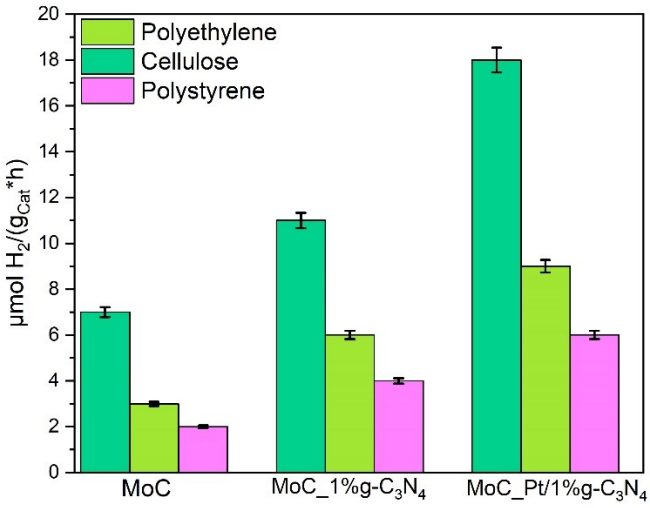


Figure 1 Comparison among different investigated systems

References

1. M. Ashraf, N. Ullah, I. Khan, W. Tremel, S. Ahmad, M. Tahir, Chemical Reviews **2023**,123,4443-4509
2. M.T. Armeli Iapichino, R. Fiorenza, V. Patamia, G. Floresta, A. Gulino, M. Condorelli, G. Impellizzeri,G. Compagni, S. Scirè, Catalysis Communications **2024**,187,106850
3. S.F. Ahmed, M. Mofijur, S. Nuzhat, N. Rafa, A. Musharrat, S.S. Lam, A. Boretti,International Journal of Hydrogen Energy **2022**,47, 37227-37255
4. Y. Zou, D. Ma, D. Sun, S. Mao, C. He, Z. Wang, J. Shi, Applied Surface Science **2019,**473,91-101
5. S.A. Balsamo, R. Fiorenza, M.T Armeli Iapichino, F. Lopez-Tenllando, F.J. Urbano,S. Scirè,Molecular Catalysis **2023**,113346

Acknowledgements

The authors thank the European Union (NextGeneration EU) MUR-PNRR project SAMOTHRACE (ECS00000022).

Probing the Metal/Oxide Interface of $IrCoCeO_x$ in $N_2H_4 \cdot H_2O$ Decomposition: An Experimental and Computational Study

Ilaria BARLOCCO[1], Silvio BELLOMI[1], Marta STUCCHI[1], Laura Prati[1], Davide FERRI[2] and Alberto VILLA[1]
[1] *Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, I-20133 Milano, Italy.*
[2] *PSI Center for Energy and Environmental Sciences, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland.*
** Ilaria.barlocco@unimi.it*

Significance and Relevance

This work aims to disclose the complex mechanism at the metal/oxide interface in boosting the hydrogen production from hydrous hydrazine in presence of NaOH. To this end, cobalt-ceria oxides doped with Ir where used as a catalyst in this reaction. A complete characterization combined with robust computational modelling was employed to unveil the processes at the Ir/Co interfaces. Moreover, the role of NaOH was studied operando with ATR-IR. We expect these results to help designing and adapting catalytic systems with improved performances in nitrogen hydrides decomposition, positively impacting the mild-CO-free H_2 production.

Preferred and 2nd choice for the topic: (1st) H_2 storage and transportation, green H_2 production, hydrogen vectors (2nd) Fundamental advances in understanding catalysis.
Preferred presentation: Oral preferred

Introduction and Motivations

Liquid Hydrogen Carriers (LHCs) are chemical compounds easily storable and transportable with a high intrinsic hydrogen content, which can be released at mild conditions. Many LHCs exist, but the need to reduce net carbon emissions has led to a focus on nitrogen-hydrides. In particular, hydrous hydrazine ($N_2H_4 \cdot H_2O$) possesses a hydrogen content as high as 8 wt.%, and its decomposition produces either molecular hydrogen and nitrogen or ammonia and nitrogen, which is the thermodynamically favoured process.[1] Great efforts have been made to improve the catalytic activity and selectivity of catalysts for this reaction. Non-noble metals (Ni, Co, Fe) present high selectivity at the cost of lower catalytic activity[2], whereas noble metals, such as Ir, Ru and Pt, are well known for their high catalytic activity but rather low selectivity. In recent years, noble/non-noble bimetallic systems have attracted interest, achieving high catalytic activity and enhanced selectivity.[3] Furthermore, although no clear mechanistic explanation is present in the actual literature, the presence of NaOH in the reaction mixture is known to increase the activity and enhance the H_2 production.[4]

Herein, an iridium–cobalt–cerium ($IrCoCeO_x$) composite was synthesized and compared to $CoCeO_x$, CeO_2, and $IrCeO_2$ to probe the performance of the metal-oxide interfaces in batch $N_2H_4 \cdot H_2O$ decomposition. The combination of kinetic batch results, comprehensive characterization by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), and HR-TEM and density functional theory (DFT) help us elucidate the role of Ir/CoO interfaces in boosting $N_2H_4 \cdot H_2O$ decomposition and promoting H2 production. Moreover, operando attenuated total reflectance infrared (ATR-IR) analysis was employed to investigate the nature of adsorbates at the solid–liquid interfaces of $IrCoCeO_x$. The formation of Co-hydroxyl and -imido species was directly correlated to the enhanced H_2 productivity through preferential breakage of the N–H bond of $N_2H_4 \cdot H_2O$ due to NaOH.

Results and Discussion

From the kinetic experiments, see Figure 1a, we observed that the catalyst is active only when Co is present. Moreover, the presence of Ir clearly boosted the performances, resulting in a 5-fold increasing of catalytic activity. The effect of NaOH was also demonstrated for IrCoCeOx comparing the reaction performed in aqueous NaOH and pure H_2O, see Figure 1b. Here, the effect of the base is clear in enhancing the activity and H_2 selectivity. The combination of different characterization techniques (i.e. XPS, CO-DRIFT and XANES) and especially the tandem analyses of the FT-EXAFS (Figure 1c) signal

revealed a Co-Ir charge transfer. Considering the complete inactivity of the Ir/CeO_2, we attributed the performances enhancement to such interaction. This was also confirmed by density functional theory calculation, using NH_3 as a probe molecule to investigate the active sites. Mechanistic insights on the role of NaOH at the Ir/CoO interface were obtained through operando ATR-IR. NaOH operates on the catalyst surface, enhancing the cooperation between vicinal Brønsted basic (Co−O−Co) and Lewis acidic (O−Co−O) sites of the Ir/CoO interface, inducing a preferential breakage of the N−H bond, i.e., higher H_2 productivity, through Co hydroxyls and imido groups, see Figure 1d.

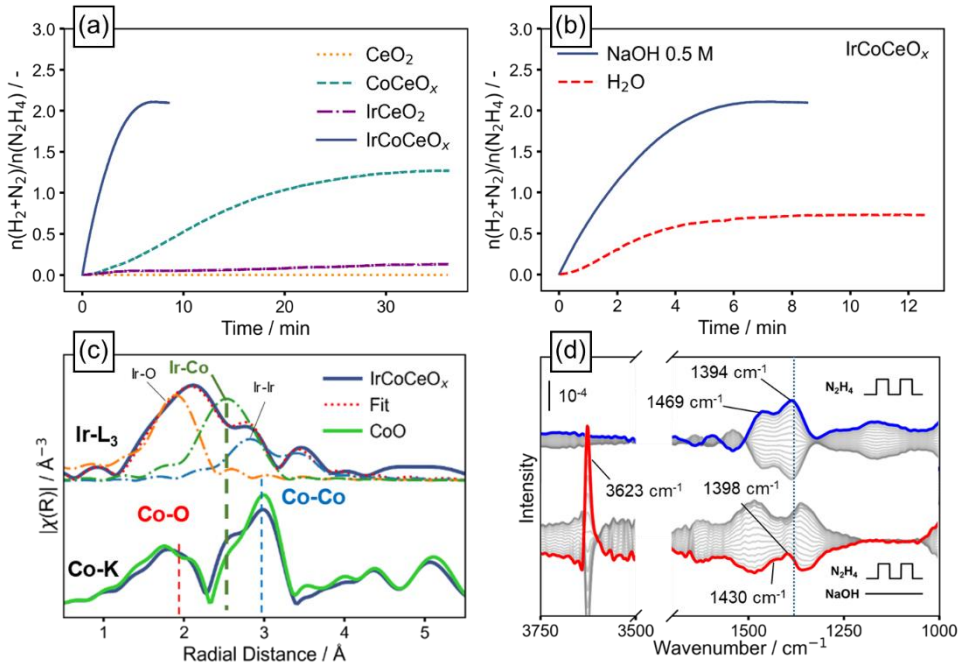


Figure 1. Kinetic profiles for the batch $N_2H_4{\cdot}H_2O$ decomposition reaction: ***(a)*** Comparison between catalysts (NaOH 0.5 M) and ***(b)*** Effect of NaOH on IrCoCeO*x*. ***(c)*** *k*2-weighted Ir−L3 and Co−K edge phase shift corrected FT-EXAFS of IrCoCeO*x* and ***(d)*** Phase resolved ATR-IR spectra from modulation experiments of $N_2H_4{\cdot}H_2O$ decomposition on IrCoCeO*x* in water (blue) and 5:1 mol/mol of NaOH (red).

In conclusion, two different take home messages emerge from this study: (1) CoOx is the active phase of the catalyst, and Ir induces an enormous increase in the activity and H_2 selectivity, (2) the presence of NaOH can greatly enhance the catalytic properties of the material. In our case this effect is due to concerted role of vicinal Brønsted basic and Lewis acidic sites, which induces a higher H_2 selectivity due to the preferential breakage of the N-H bond of hydrazine.

References

1 P. X. Zhang, *Catal. today* **2011**, *165*, 80–88.
2 L. He, *Acs Catal.* **2015**, *5*, 1623–1628.
3 N. Cao, *Inorg. Chem.* **2014**, *53*, 10122–10128.
4 H. Wang, *Catal. Commun.* **2017**, *100*, 33–37.

Acknowledgements

This work has been partially supported from Italian Ministerial grant PRIN 2022 “Green hydrogen from urea-rich wastewater using novel catalytic processes.”--PRIN202223AVILL_01.

Iron catalyst for CH_4 pyrolysis: characterizing C formation to understand catalyst deactivation

Lidia CASTOLDI[1], Veronica PIAZZA[1], Chiara NEGRI[1], Marco ORSENIGO[1], Davide CAFARO[1], Matteo MAESTRI[1], Gianpiero GROPPI[1], Alessandra BERETTA[*,1]

[1]*Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, Via La Masa, 34 – 20156 Milano, Italy.*

** alessandra.beretta@polimi.it*

Significance and Relevance

Methane pyrolysis represents a potential route to H_2 production with direct sequestration of solid C. Iron-based catalysts are active and robust, but the increasing accumulation of carbon is accompanied by rapid loss of activity. Yet, maximizing the C-capacity is a key factor behind process development. This work examines Fe/Al_2O_3 catalysts at high Fe load and investigates the compositional effects, the role of reduction, the transformations that follow the incipient and extensive formation of C to better elucidate the carbon build-up chemism and obtain rational guidelines to scale-up and industrialization.

Preferred and 2nd choice for the topic: Fundamental advances in understanding catalysis; H_2 storage and transportation, green H_2 production, hydrogen vectors
Preferred presentation: Oral preferred

Introduction and Motivations

Catalytic methane pyrolysis ($CH_4 \rightarrow 2\ H_2 + C$, $\Delta H° = 75.6$kJ/mol) to produce CO_x-free hydrogen is receiving more and more attention as a solution to meet the goals of decarbonization. Temperatures above 1000°C are needed with C-based catalysts or in thermal processes, but the use of metal-based catalysts (as Fe, Ni, and Co) allows to obtain appreciable methane conversions in the range of 700-900°C. Due to the still severe temperatures, active catalysts also call for proper textual properties [1].

In this work, iron-based catalysts with Al_2O_3 as a textural promoter have been prepared, characterized, and tested in methane pyrolysis. The research focus has been on the chemism of C-formation from Fe/Fe_3C to better understand the deactivation law and the overall C-load capacity. Besides, the final morphology and reactivity of the spent catalyst were characterized, in view of the open final destiny, which might involve C-valorization and/or underground storage.

Materials and Methods

Fe/Al_2O_3 catalysts with variable Fe/Al molar ratios were prepared by the fusion-decomposition (FD) method, after Pinilla et al.[2]: iron nitrate and aluminum nitrate are mixed and calcined at 350°C for 1 h, to promote the thermal decomposition of nitrates, and subsequently to 450°C for 8 h, to promote the formation of their respective oxides. Catalysts were also reduced according to the suggested procedure, with a maximum reduction temperature of 550°C to preserve the Fe-surface.

Experiments of catalytic CH_4 pyrolysis were carried out in thermobalance under temperature ramp (TG/MS, catalyst load 5 mg), but also in packed bed reactor (catalyst load 0.75 g) and in fluidized reactor (catalyst load = 3-5 g). Fresh, reduced and C-loaded catalysts were characterized by BET, XRD, (HR)-SEM, HR-TEM, TPR, and TPO.

Results and Discussion

The results herein reported focus on the 1:1=Fe:Al molar ratio, since this formulation was especially active and prone to high C-loading. The surface area amounted to about 100 m^2/g_{cat}; XRD highlighted a well-defined crystal structure, mainly associated with hematite phase (Fig. 1A, fresh catalyst). In conventional H_2-TPR, two major reduction stages were seen below 600°C and were ascribed to $Fe_2O_3 \rightarrow Fe_3O_4$, and $Fe_3O_4 \rightarrow FeO \rightarrow Fe^0$ transformations. At 900-1000°C a minor and broad H_2 consumption was ascribed to the reduction of $FeAl_2O_4$, resulting from the reactions between Fe_3O_4, FeO, Fe^0, and Al_2O_3. However, the reduction protocol (used in the reactor) up to 550°C with hold in pure H_2 was

effective in obtaining Fe^0; indeed, H_2-TPR after such reduction process showed that only a minor high temperature consumption of H_2 related to the iron aluminate occurs.

The formation of metallic α-Fe and $FeAl_2O_4$ is evident in the XRD pattern, with an estimated Fe-size of 30 nm (Fig. 1A, reduced samples). FESEM and TEM images of fresh catalyst reveal flat islands of Al_2O_3 over which iron is dispersed; the presence of α-Fe and $FeAl_2O_4$ in the reduced sample is confirmed by the calculation of the interplanar distance. In the TG/MS experiment (Fig. 1B), the initial reduction phase is consistent with the TPR studies. Once CH_4 is added, an increase of the sample weight is observed due to the C formation and accumulation following the pyrolysis reaction (Fig. 1B). The weight gain (i.e. the reaction rate) is very high at the beginning, then it declines with time and C-load. The heterogeneous morphology of the catalysts where Fe aggregates are readily accessible might be the key behind the capability to grow C-structures that greatly exceed the pore volume.

Catalysts at different C-loads were obtained also from pyrolysis tests in packed bed and fluidized bed reactors. Importantly, a generalized deactivation law was deduced from the kinetic analysis of the CH_4 pyrolysis tests, such that the catalyst activity is uniquely dependent on the specific C-load and on temperature. We expect thus that the characterization of spent catalysts obtained from very different reacting and reactor conditions (but same temperature) and largely varying C-load provide a pathway through the surface transformations. XRD of spent catalysts showed that iron is present mainly as Fe_3C, and the initial α-Fe decreases in intensity as the reaction proceeds (i.e. as the C loading increases); at the same time the reflex attributed to graphitic carbon grows. $FeAl_2O_4$ is not long present, probably reduced to Fe^0 by carbon. FESEM and TEM confirmed the presence of Fe_3C and ordered C structures with a tubular structure (i.e. nanotubes, $d_{average}$ 50nm ca.); Raman spectra also suggested a highly ordered structural morphology for the carbon (I_G/I_D ratio > 2).

It is inferred that C structures are formed by precipitation from the C-soluble Fe_3C phase, while the residual Fe content governs the actual rate of reaction. The mechanism of Fe deactivation thus would pass through its progressive conversion and desegregation into Fe_3C particles. Fe aggregate size of the initial reduced catalyst might play an important role, which is currently under investigation by the analysis of the effect of Fe load and preparation procedures.

Regeneration experiments were carried out on the spent catalysts. Gasification tests showed that O_2 can react with solid C at 340°C, suggesting accessibility of Fe/Fe_3C sites despite significant C coverage; similarly, CO_2 gasified solid C (reverse Boudouard reaction) at 630°C, aligning with typical non-noble metal catalyst activity like dry reforming. Instead, steam gasification tests required around 740°C for solid C conversion, with high rates suggesting a higher activation energy compared to CO_2 gasification.

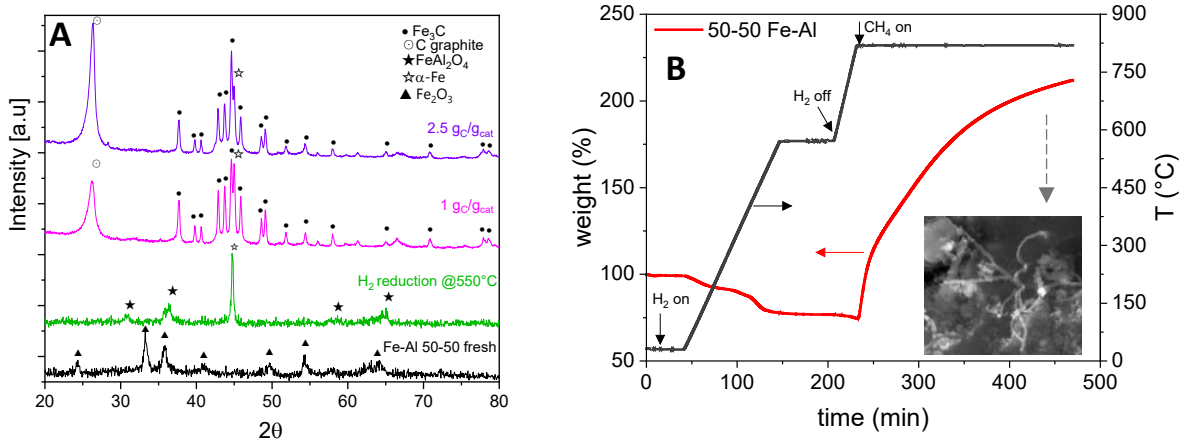


Figure 1 A) XRD pattern of fresh, H_2 reduced, spent catalyst; B) TG/MS analysis of reduction and CH_4 pyrolysis over fresh catalyst with SEM image of spent catalyst.

References

1. J.K. Krummenacher, K.N. West, L.D. Schmidt, *Journal of Catalysis* **2003**, 215, 332–342.
2. J.L. Pinilla, R. Utrilla, R.K. Karn, I. Suelves, M.J. Lázaro, R. Moliner, A.B. García, J.N. Rouzaud, *International Journal of Hydrogen Energy* **2011**, 36, 7832-7843

Facile coating of reduced graphene oxide and TiO_2 on floating polyurethane foams for photocatalytic water decontamination

Anna DOTTI[1]*, Andrea BASSO PERESSUT[1], Roberto MATARRESE[2], Saverio LATORRATA[1]
[1]*Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Piazza Leonardo da Vinci 32, 20133, Milano, Italy.*
[2]*Politecnico di Milano, Dipartimento di Energia, Via Lambruschini 4, 20156, Milano, Italy.*
** anna.dotti@polimi.it*

Significance and Relevance

We developed a simple methodology to deposit a binder-free, aqueous-based coating containing reduced graphene oxide and TiO_2 onto polyurethane floating foams. The deposition only involves dip coating, compressed air blowing, and drying at 40 °C. Exposed to UV-Vis light, coated foams completely remove Rhodamine B from water in 90 min. The dye is firstly adsorbed and subsequently photodegraded on the foam surface. This study represents a novel approach to immobilize TiO_2 for photocatalytic water treatment, using commercial materials and a simple, low energy-consuming method. TiO_2 photoactivity is not only preserved, but possibly enhanced by the combination with reduced graphene oxide.

Topic: Water treatment *(preferred)*; Photocatalysis and photoelectrocatalytic approaches (*2nd choice)*
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

TiO_2 is the most studied and used photocatalyst. However, its practical application in water treatment is still limited because: i) its 3.2 eV bandgap requires UV light, implying a significant energy consumption, ii) it is mainly employed as nanopowder, which tends to agglomerate, and is hardly recoverable after use[1]. Coupling TiO_2 with reduced graphene oxide (rGO) allows to reduce the material bandgap, improve the separation of charge carriers, and, being rGO an excellent adsorbent, keep contaminants in direct contact with the photocatalyst[2]. Because of its self-assembling properties, rGO can also be effective for immobilizing TiO_2 nanoparticles in macroscopic objects, as already demonstrated by our research group[3].

Materials and Methods

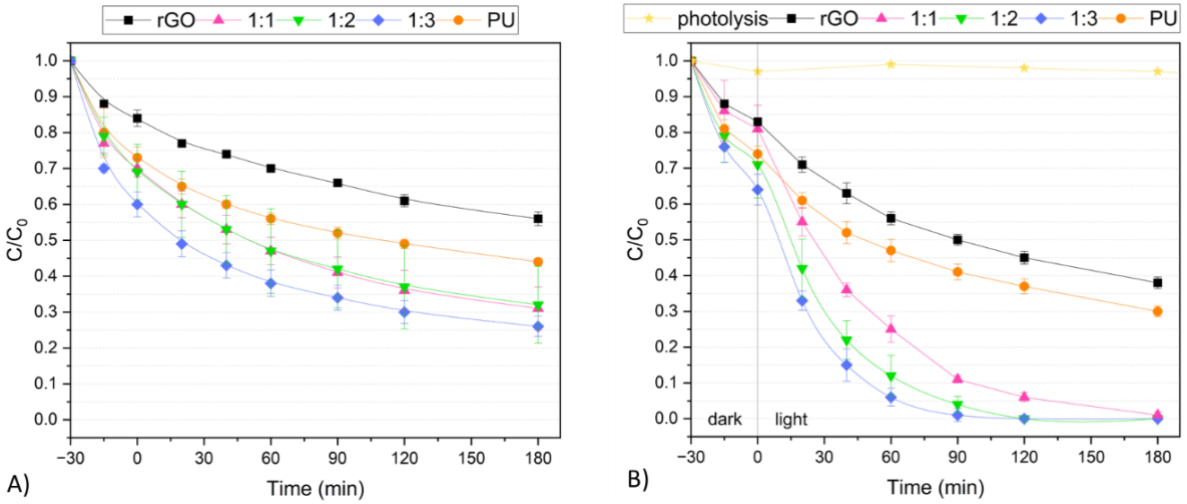
The slurry for the coating procedure was prepared by stirring at ambient temperature: i) a commercial graphene oxide (GO) aqueous dispersion, ii) ascorbic acid as reducing agent for GO, iii) TiO_2 Degussa P25. GO:TiO_2 mass ratios of 1:1, 1:2 and 1:3 were considered. A commercial polyurethane (PU) 20 PPI foam, cut into 0.5 cm-thick cylinders of 5.5 cm diameter, was used as substrate, without any pre-treatment. Foams were dip-coated, blown with compressed air to remove the excess coating, and dried at 40 °C for 2 h. For water decontamination tests, each foam was contacted with 100 mL of a 3 mg/L Rhodamine B (RhB) aqueous solution. The light source was a UV-Vis Osram Ultra Vitalux 300 W lamp. RhB concentration was monitored with UV-Vis spectroscopy.

Results and Discussion

Foams coated with rGO/TiO_2 1:1, 1:2, and 1:3 (w:w) were employed in decontamination tests both in dark and light conditions, comparing their behavior with the one of bare PU and rGO-coated foams. Experiments in dark (Fig. 1A) highlight that all the samples have a significant RhB adsorption capacity, reaching 55% of removal with bare PU, and 70-75% of removal with rGO/TiO_2-coated foams after 180 min. Different results were obtained by exposing the samples to light (Fig. 1B). Curves related to rGO/TiO_2-coated foams exhibit a marked change in the slope at 0 min, which corresponds to the activation of the UV-Vis lamp, after 30 min in dark. This suggests the shift from a pure adsorption to a photocatalysis-dominated process, which leads to 100% removal of RhB with the 1:1-coated foam after

180 min. However, the graph clearly indicates that an increase in TiO_2 content determines an acceleration in the decontamination process. The complete RhB removal is indeed reached at 120 min using the 1:2-coated sample, and already at 90 min with the 1:3.

Figure 1. Normalized concentration of RhB during adsorption (A) and photodegradation (B) tests.



After the decontamination tests, foams were illuminated to reveal the possible presence of RhB through fluorescence. RhB can be clearly detected on all the foams employed in dark conditions. After photodegradation tests, instead, RhB is largely visible only on the rGO-coated foam. On rGO-TiO_2 coatings, limited pink areas can be seen on the 1:1 sample, which completely disappear as the TiO_2 content increases. Thus, it can be hypothesized that RhB is firstly removed from water by adsorption on the foams surface, and successively photodegraded. Accordingly, after 180 min of test under light RhB can still be detected on the 1:1-coated foam, which features a slower degradation kinetics than 1:2 and 1:3-coated samples.

Foams were then immersed in deionized water, to assess the possible release of RhB. rGO-coated foams, both after adsorption and photodegradation tests, determine a slight water contamination with RhB, reaching the maximum after 24 h. However, the amount of released dye is remarkably lower than the one previously removed. The same behaviour was registered for the 1:3-coated sample used in dark conditions. The 1:3 foam employed in experiments under illumination, instead, does not release any RhB, even after 72 h.

The obtained results provide multiple confirmations of the photodegradation ability of TiO_2-containing coatings. An increase in the TiO_2 content determined a faster RhB removal, thus new coating formulations with a higher quantity of TiO_2 will be possibly prepared. Also, the photodegradation activity of coated foams will be assessed toward other organic contaminants, e.g. drugs or pesticides.

References

1. J. A. Rengifo-Herrera, C. Pulgarin, *Chemical Engineering Journal* **2023**, 477, p. 146875.
2. G. Luna-Sanguino, A. Ruíz-Delgado, A. Tolosana-Moranchel, L. Pascual, S. Malato, A. Bahamonde, M. Faraldos, *Science of The Total Environment* **2020**, 737, p. 140286.
3. A. Basso Peressut, C. Cristiani, G. Dotelli, A. Dotti, S. Latorrata, A. Bahamonde, A. Gascò, D. Hermosilla, R. Balzarotti, *Nanomaterials* **2023**, *13*(6), p. 1043.

Nanoceria as acid-base catalyst for hydrolysis of sulfonamides, sulfonylureas and other emerging pollutants

Jan ČUNDRLE[1], Martin ŠŤASTNÝ[1], Jakub EDERER[2], Pavel JANOŠ[2], Jiří HENYCH[*,1]
[1]*Institute of Inorganic Chemistry of the Czech Academy of Sciences, 250 68 Husinec-Řež, Czechia.*
[2] *Jan Evangelista Purkyně University in Ústí nad Labem, Faculty of Environment, Pasteurova 3632/15, 400 96 Ústí nad Labem, Czechia.*
** henych@iic.cas.cz*

Significance and Relevance

Nanoceria can be used as an efficient acid-base heterogeneous catalyst for the hydrolytic decomposition of various ester compounds including emerging water pollutants such as organophosphate pesticides. In recent works, we have shown that many other environmentally relevant compounds such as sulfonamide antibiotics or bisphenol-S can also be spontaneously decomposed at ambient conditions using nanoceria. We propose that the cleavage of other important bonds in biologically and environmentally important organic molecules can be achieved using a carefully designed and prepared ceria catalyst.

Preferred and 2nd choice for the topic: Water treatment, photocatalysis
Preferred presentation: (Oral preferred or Short Oral)

Introduction and Motivations

Degradation of various environmental pollutants in water and air using nanomaterials is an attractive way to remove many micropollutants and contaminants of emerging concern (CEC) including pesticides, industrial chemicals or antibiotics. Several transition metal oxides (TMO) show extraordinary surface reactivity, catalytic, photocatalytic and electrocatalytic activities that can be used in various water and air treating systems.

Nanoceria is a promising reducible metal oxide with exceptional redox and acid/base properties, with many industrial and emerging applications including VOC oxidation in three-way catalyst, fuel cells, or water-gas shift reaction.[1] In addition, it can also spontaneously degrade phosphate (and other) esters,[2] enabling the decontamination of organophosphate pesticides or nerve agents.[3] However, its hydrolytic activity can extend far beyond dephosphorylation reactions and can be useful for many other environmentally and biologically relevant catalytic reactions.[4]

Materials and Methods

Various nanoceria samples with the different structural and surface chemical properties were prepared by several water-based precipitation methods using cerium nitrate hexahydrate as starting compound. The synthesis details are available elsewhere.[5] One of the precipitation methods was also used to prepare ceria/graphene oxide composites.[6] The kinetics and mechanism of hydrolytic and photocatalytic degradation of several environmental pollutants (sulfonamide antibiotics, bisphenols) on the ceria surfaces were studied by HPLC/DAD, LC/MS-MS and NMR spectroscopy.

Results and Discussion

In our recent study[5], it was experimentally demonstrated for the first time that CeO_2 nanostructures show extraordinary reactivity toward sulfonamide drugs (sulfadimethoxine, sulfamerazine, and sulfapyridine) in aqueous solution without any illumination, activation, or pH adjustment. Hydrolytic cleavage of various bonds, including S–N, C–N, and C–S, was proposed as the main reaction mechanism and was indicated by the formation of various reaction products, namely, sulfanilic acid, sulfanilamide, and aniline, which were identified by HPLC-DAD, LC-MS/MS, and NMR spectroscopy (Figure 1). The degradation efficiency was strongly dependent on the structure of the sulfonamide molecule and physicochemical properties of nanoceria. However, not all tested sulfonamide drugs were spontaneously decomposed (e.g., sulfomethoxazole), indicating an urgent need for further elucidation

of the reactivity of cerium along with identification of active sites and other key parameters that control the decomposition reactions on the ceria surfaces.

Furthermore, the composites based on CeO_2 nanoparticles grown in situ on graphene oxide (GO) sheets were prepared by a low-temperature water-based method and used for the removal of bisphenols from water.[6] It has been demonstrated that ceria-based nanomaterials can also spontaneously decompose bisphenol-S (BPS) containing a sulfonyl functional group by hydrolytic cleavage upon its adsorption, while bisphenol-A (BPA) and F (BPF) can be efficiently decomposed by simulated solar light using CeO_2/GO composites as photocatalysts.

Based on these results, further tests are underway with other pollutants (e.g., sulfonylurea herbicides) and molecules with ester (or other) bonds that can undergo hydrolysis on the surface of nanoceria. It can be assumed that these reactions can find application in heterogeneous catalysis and environmentally significant degradation reactions and may be relevant for other nanocrystalline transition metal oxides.

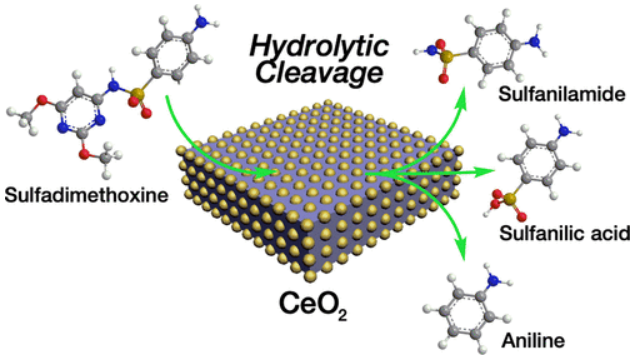


Figure 1 Nanoceria can decompose various sulfonamide antibiotics (e.g., sulfadimethoxine) on their surface by hydrolytic cleavage under ambient conditions to form various degradation products such as sulfanilamide, sulfanilic acid, or aniline.

References

1. T. Montini, M. Melchionna, M. Monai, P. Fornasiero, *Chem. Rev.* **2016**, *116(10)*, 10222-10234.
2. S. Bhasker-Ranganath, Y. Xu, *ACS Catal.* **2022**, *12(16)*, 10222-10234.
3. Z. Tan, T-S. Wu, Y-L. Soo, Y-K. Peng, *Appl. Catal. B: Environ.* **2020**, *264*, 118508.
4. M. Zhang, S. Zhang, Z. Qi, M. Xie, Y. Qu, *Catal. Sci. Technol.* **2024**, *14*, 225-240.
5. J. Henych, M. Šťastný, S. Kříženecká et al., *Inorg. Chem.* **2024**, *63(4)*, 2298-2309.
6. M. Šťastný, D. Bavol, J. Tolasz, et al., *Environ. Sci.: Nano.* **2025**, *DOI: 10.1039/D4EN00787E*.

Acknowledgements

The research was supported by Czech Science Foundation (GAČR) Grant No. 25-15972S.

Efficient palladium recovery and catalyst development from electroplating wastewater using functionalized carbon materials

Elena MARIANI[1,2,3,*], Marco BONECHI[1,2], Ilaria MAGGINI[1], Claudia GIOVANI[1], Leonardo LARI[4,5], Matteo SAVASTANO[2,6], Claudio FONTANESI[2,7], Antonio BIANCHI[1], Massimo INNOCENTI[1,2]

[1] *Department of Chemistry, UNIFI, via della Lastruccia 3, 50019 Sesto Fiorentino, Italy.*

[2] *INSTM, via Giuseppe Giusti, 9, 50121 Florence, Italy.*

[3] *Eco-Tech Finish s.r.l., Z.I. San Zeno, Strada C 27, 52100 Arezzo, Italy.*

[4] *School of Physics, Engineering and Technology, University of York, Heslington, York YO10 5DD, UK.*

[5] *The York-JEOL Nanocentre, University of York, Heslington, York YO10 5BR, UK.*

[6] *Department of Human Sciences, University San Raffaele, Via di Val Cannuta 247, 00166 Rome, Italy.*

[7] *Department of Engineering, University of Modena and Reggio Emilia, via Vivarelli 10, 41125 Modena, Italy.*

** elena.mariani@unifi.it*

Significance and Relevance

The study demonstrates an innovative approach for recovering palladium (Pd) from electroplating wastewater using functionalized carbon materials, such as carbon black and graphene. These materials, modified with a pyrimidine TREN derivative, exhibit high Pd recovery rates (up to 97% within 24 hours) under eco-friendly conditions. The recovered Pd forms hybrid materials that serve as efficient catalysts for the Oxygen Reduction Reaction (ORR) in alkaline media, achieving a catalytic activity comparable to commercial platinum electrodes. This work is novel in combining wastewater recovery with the production of cost-effective, sustainable electrocatalysts, promoting circular economy principles.

Preferred and 2nd choice for the topic: Water treatment; Sustainable and clean energy production and transport

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The study addresses the dual challenges of resource sustainability and industrial wastewater management, focusing on palladium (Pd) recovery from electroplating processes. Precious metals like Pd, critical for industrial and green technologies, face supply limitations and high costs, necessitating efficient recovery methods[1]. Traditional approaches are energy-intensive and often unsuitable for low-concentration solutions[2]. Electroplating rinse waters, typically neglected, offer a valuable recovery opportunity, aligning with circular economy goals[3]. Functionalized carbon materials have shown promise in capturing and repurposing Pd, reducing waste while enabling the creation of effective catalysts for energy applications[4,5].

Materials and Methods

Carbon black (CB) and graphene (G1) were functionalized with a pyrimidine TREN derivative (HL) to enhance Pd recovery. Recovery experiments used a Pd(II) solution (0.1 g/L) with functionalized and non-functionalized carbons, followed by quantification via MP-AES. Structural and chemical analyses included SEM, STEM, EDS, and XPS. Catalytic properties were assessed through electrochemical techniques (CV, LSV, and RRDE) in alkaline media. The materials were tested for their Oxygen Reduction Reaction (ORR) performance, focusing on parameters like onset potential, half-wave potential and the number of exchanged electrons.

Results and Discussion

The recovery of precious metals in the electroplating industry presents both economic and environmental challenges. While various methods have been proposed for treating spent electrolyte solutions, limited attention has been given to recovering metals from washing processes following metal deposition. This study focuses on evaluating the effectiveness of two carbon materials, CB and G1, in recovering palladium from washing water produced during electrochemical palladium

deposition. CB and G1 exhibit favorable properties for palladium recovery and catalyst production, including high surface area, reactive surface groups, and excellent electrical conductivity. The findings demonstrate a novel approach for palladium recovery from aqueous solutions while simultaneously developing low-cost materials for alkaline fuel cell catalysts. Additionally, the potential functionalization of CB and G1 with a pyrimidine TREN derivative ligand was explored. This ligand promotes palladium recovery through chemical complexation and creates heterogeneous single-atom catalytic sites. The functionalized materials showed catalytic properties comparable to those required for the Oxygen Reduction Reaction (ORR). Rotating ring-disk electrode tests revealed that the number of electrons exchanged per O_2 molecule was close to 4, indicating nearly complete conversion of O_2 to H_2O. These promising results were achieved using heterogeneous catalysts containing only 5.21 wt% of recovered palladium, demonstrating the potential for advancing eco-friendly electroplating processes and developing efficient, low-content platinum-group metal (PGM) carbon-based catalysts.

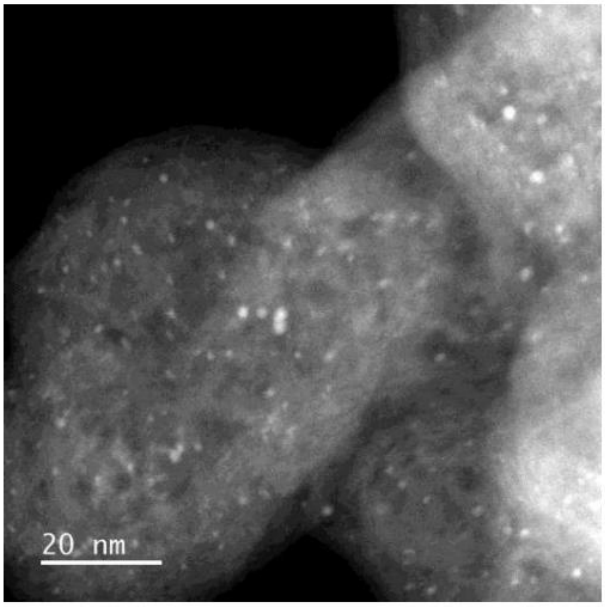


Figure 1 HAADF STEM images of raw carbon materials obtained after the recovery process of palladium. Pd nanoparticles are visible as bright spots, support coverage is very uniform.

References

1. European Commission, Directorate General for Internal Market, Industry, Entrepreneurship and SMEs, *Publications Office*, **2020**, https://data.europa.eu/doi/10.2873/58081.
2. W. Giurlani et all, *Sustainability*, **2024**, *16*, 5821.
3. S. Massari, M. Ruberti, *Resources Policy*, **2013**, *38*, 36-43.
4. E. H. Sujiono et all, *Results in Chemistry*, **2022**, *4*, 100291.
5. M. Bonechi et all, *Catalysts*, **2021**, *11*, 764.

Acknowledgements

The authors acknowledge 1) Fondazione CR Firenze, Fondazione per la Ricerca e l'Innovazione dell'Università degli Studi di Firenze and Confindustria Firenze within the FABER 4 project; 2) Regione Toscana PR FESR 2021/2027, Azione 1.1.4.1, Bando 2 "Progetti di ricerca e sviluppo per le MPMI e Midcap" which made possible the project "Processo Unificato su Leghe di zama, ottone e alluminio, Sicuro e Ecofriendly" (P.U.L.S.E) CUP-ST 27717.29122023.043000271; 3) Project 2022NW4P2T CUP B53D23013890006 "From metal nanoparticles to molecular complexes in electrocatalysis for green hydrogen evolution and simultaneous fine chemicals production (FUTURO)" PRIN2022 Progetti di Ricerca di Rilevante Interesse Nazionale funded by the Italian Ministry of University and Research and NextGenerationEU.

Bacterial Disinfection from Selected Water Pathogens Using an Iron-doped TiO_2 Photocatalyst Under Visible Light

Najeebullah CHANNA*[1], Francesca Stefania FREYRIA[1], Tanveer A. GADHI[2], Alessandro CHIADÒ[1], Nicola BLANGETTI,[1] Barbara BONELLI[1]

[1] *Department of Applied Science and Technology, Corso Duca degli Abruzzi 24, Politecnico di Torino,10129 Torino, Italy.*

[2] *US-Pakistan Center for Advanced Studies in Water (USPCASW), Mehran University of Engineering and Technology, Jamshoro, 76062, Pakistan.*

** najeebullah.channa@polito.it*

Significance and Relevance

TiO_2 is a widely used photocatalyst for water treatment and pollutants degradation,[1] but is active under UV light due to its bandgap in the 3.0 – 3.4 eV range. Doping with iron (a non-toxic metal) can reduce the bandgap, allowing for a better exploitation of the solar spectrum in the visible range. Current treatment methods like chlorination and UV irradiation may result in the formation of toxic by-products. So far, few studies deal with the disinfection of pathogenic bacteria by Fe-doped TiO_2. This study is related to the use of an Fe-doped TiO_2 obtained by a sol-gel method in the photocatalytic disinfection from *E. coli* and *S. aureus* under visible light produced by a commercial lamp.

Preferred presentation: Oral preferred or Short Oral.

Introduction and Motivations

Bacterial contaminated drinking water may cause serious health problems.[2] For instance, *E. coli* and *S. aureus* found in contaminated water are responsible for several waterborne diseases.[3] Specifically, *E. coli* is considered the indicator bacteria in contaminated drinking water and indicates the contamination source in the drinking water system. Conventional disinfection treatment methods such as chlorination, ozonation, and UV are expensive methods and could produce toxic by-products during disinfection.[4] Therefore, effective alternative methods are needed to disinfect the waterborne pathogenic bacteria from drinking water. In this respect, photocatalytic treatment could be an alternative disinfection method. In this study, Fe doped TiO_2 was synthesized and then tested for disinfection of two Gram-negative and Gram-positive bacteria, respectively *E. coli* and *S. aureus*.

Materials and Methods

The Fe doped TiO_2 photocatalyst was synthesized by a sol-gel method[5], along with an undoped TiO_2, used for comparision. The nanomaterials were characterized through different techniques such as XRD, Diffuse Reflectance (DR) UV–vis spectra, BET, FESEM, and Zeta potential.

The two bacterial strains *E. coli* (ATCC 8739) and *S. aureus* (ATCC 25923)[6] were selected for disinfection experiments with the initial concertation of 10^4 CFU/mL, the photocatalytic disinfection experiments were performed in different conditions in the dark and under the light irradiation, with a catalyst dose of 1 g/L. The disinfection experiments were performed under light and control conditions (in dark: bacteria and photocatalytic nanoparticles and in light: only bacteria). The bacterial disinfection at different times was monitored through the plate count method.

Results and Discussion

The XRD patterns show all the observed peaks were ascribed to the TiO_2 anatase phase in both undoped and Fe-doped TiO_2. The bandgap was evaluated by applying Tauc's plot method for indirect semiconductors (i.e. by plotting $(F(R)*h\upsilon)^{1/2}$ vs Energy, eV) the corresponding Tauc's plot from which the band gap of Fe-TiO_2 undoped TiO_2 resulted to be 2.80 eV and 3.34 eV, respectively.

The Specific Surface Area (SSA), as obtained by applying the BET (Brunauer–Emmett–Teller) method, of Fe-TiO_2 was 123 m^2/g, i.e. slightly higher than undoped TiO_2 (116m^2/g)

The bacterial disinfection for *E. coli* (99.9%), and *S. aureus* (99.8%) was obtained under visible light irradiation with both bacteria in the presence of Fe-TiO_2 whereas the activity of undoped TiO_2 was much lower, due to its different optical properties. No significant Log reduction was observed in control samples. During photocatalytic disinfection in the presence of Fe-TiO_2 reactive oxygen species (i.e. O_2- and OH• radicals) were produced, which are responsible for inactivating the bacteria by damaging the cell wall or membrane, according to previous studies[7].

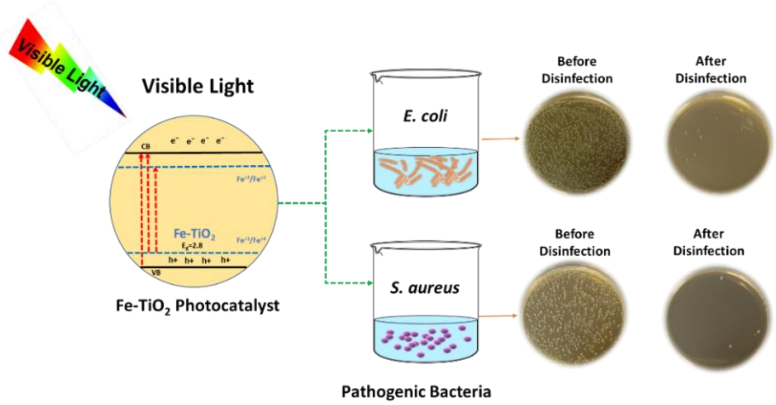


Figure 1. Photocatalytic disinfection mechanism and bacterial reduction on agar plates before and after photocatalytic treatment

Figure 1. The overall mechanism of generating radical ionic species from the photocatalyst surface and their reaction with bacterial cell walls and membranes for their inactivation as depicted from very few bacterial cells on the agar plate after photocatalytic treatment.

In conclusion, Fe-TiO_2 photocatalyst shows the potential to inactivate pathogenic bacteria (99.9%) and could reduce the health risk of waterborne diseases.

References

The article "Channa et al. Photocatalytic disinfection of selected waterborne pathogens by visible light-active manometric iron-doped TiO_2 obtained by sol-gel method" under review in the (ACS Applied Nano Materials).

(1) Anucha, C. B.; Altin, I.; Bacaksiz, E.; Stathopoulos, V. N. Titanium Dioxide (TiO_2)-Based Photocatalyst Materials Activity Enhancement for Contaminants of Emerging Concern (CECs) Degradation: In the Light of Modification Strategies. *Chemical Engineering Journal Advances* **2022**, *10*, 100262. https://doi.org/10.1016/J.CEJA.2022.100262.

(2) Khatri, N.; Tyagi, S. Influences of Natural and Anthropogenic Factors on Surface and Groundwater Quality in Rural and Urban Areas. *Front Life Sci* **2015**, *8* (1), 23–39. https://doi.org/10.1080/21553769.2014.933716.

(3) Sharma, S.; Bhattacharya, A. Drinking Water Contamination and Treatment Techniques. *Appl Water Sci* **2017**, *7* (3), 1043–1067. https://doi.org/10.1007/S13201-016-0455-7.

(4) Ni, L.; Meng, J.; Li, X.; Zhang, Y. Surface Coating on the Polyamide TFC RO Membrane for Chlorine Resistance and Antifouling Performance Improvement. *J Memb Sci* **2014**, *451*, 205–215. https://doi.org/10.1016/J.MEMSCI.2013.09.040.

(5) Freyria, F. S.; Compagnoni, M.; Ditaranto, N.; Rossetti, I.; Piumetti, M.; Ramis, G.; Bonelli, B. Pure and Fe-Doped Mesoporous Titania Catalyse the Oxidation of Acid Orange 7 by H2O2 under Different Illumination Conditions: Fe Doping Improves Photocatalytic Activity under Simulated Solar Light. *Catalysts* **2017**, *7* (7). https://doi.org/10.3390/CATAL7070213.

(6) Yen, L. T.; Weng, C. H.; Than, N. A. T.; Tzeng, J. H.; Jacobson, A. R.; Iamsaard, K.; Dang, V. D.; Lin, Y. T. Mode of Inactivation of Staphylococcus Aureus and Escherichia Coli by Heated Oyster-Shell Powder. *Chemical Engineering Journal* **2022**, *432*, 134386. https://doi.org/10.1016/J.CEJ.2021.134386.

(7) Paiva, C. N.; Bozza, M. T. Are Reactive Oxygen Species Always Detrimental to Pathogens? *Antioxid Redox Signal* **2014**, *20* (6), 1000–1034. https://doi.org/10.1089/ARS.2013.5447.

Acknowledgements

The authors acknowledge Prof. Francesca Bosco and Chiara Mollea (Department of Applied Science and Technology, Politecnico di Torino) for fruitful discussion; and USPCASW, MUET, Pakistan for technical support. FSF contribution was carried out within the Agritech National Research Center and received funding from the European Union Next-GenerationEU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) – MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.4 – D.D. 1032 17/06/2022, CN00000022). This manuscript reflects only the authors' views and opinions, neither the European Union nor the European Commission can be considered responsible for them.

Study on the photodegradation of pharmaceuticals using graphitic carbon nitride derivatives

Eleonora RUSSO[*,1], Eryk FERNANDES[2], João GOMES[2], Paolo SGARBOSSA[1], Rui C. MARTINS[2]
[1]*University of Padua, Department of Industrial Engineering, via F. Marzolo 9, 35131, Padova, Italy.*
[2]*University of Coimbra, Department of Chemical Engineering, rua S. Lima, 3030-790, Coimbra, Portugal*
** eleonora.russo.2@phd.unipd.it*

Significance and Relevance

Non-conventional derivatives of graphitic carbon nitride (g-C_3N_4) doped with bromine have been synthesized for the application to wastewater photocatalytic depollution from emerging pollutants. The influence of different brominated precursors was tested: melamine bis-hydrobromide, 2-Bromobenzonitrile, and 4-Bromo-N,N dimethylaniline. As model pollutant pharmaceuticals an antibiotic (sulfamethoxazole) and a beta-blocker (atenolol) were chosen. In the case of sulfamethoxazole, the removal efficiency with four of the photocatalysts tested reached a value higher than 95% after two hours of treatment, under irradiation with a visible light lamp. In the case of atenolol, similar results were obtained.

Preferred and 2nd choice for the topic: Water treatment or photocatalysis
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Graphitic carbon nitride is a semiconductor material with stacked nanosheet structure that can be synthesized from easily applicable, economic, and eco-friendly procedures, such as thermal condensation. Nonetheless, pure g-C_3N_4 has drawbacks which limit its utilization as a photocatalyst, due to the fact that it can only absorb in the blue light region of the solar spectrum. Furthermore, it has a low specific area and fast recombination of the photogenerated election-hole pairs[1]. In order to overcome these drawbacks, some modifications such as heteroatom doping, copolymerization with non-metal compounds, deposition of noble metals, construction of heterostructures have been considered[2]. In the work by Bresolin et al. (2021)[3], the thermally induced copolymerization of melamine and 2-bromobenzonitrile was performed, producing a g-C_3N_4 derivative with a lower band gap of 2.55 eV and good photocatalytic properties in the degradation of Rhodamine-B. In this case, different doped graphitic carbon nitride materials have been synthesized. They were obtained starting from three different brominated precursors: melamine bis-hydrobromide, 2- Bromobenzonitrile, and 4-Bromo-N,N-dimethylaniline. The materials obtained were tested on the photodegradation of pollutants of emerging concerns.

Materials and Methods

Two different approaches were pursued for the thermal synthesis of the melamine mixture, namely a muffle treatment in air and in a vertical pyrolizer under inert atmosphere. In the muffle, a crucible was placed for 2h at 550 °C. The same procedure was carried out in the pyrolizer, with a N_2 constant flow of 1 mL/s, for 2h at 550 °C, aiming to make a comparison between different conditions of thermal treatment. The general testing procedure was performed as followed: 60 mg of photocatalyst were added to 200 mL of a 1 mg/L solution of pollutant to treat and stirred in a beaker. The first 30 minutes of the test were conducted in dark conditions to evaluate the adsorption effect. The system was then

irradiated with visible light. Samples of the solution were analyzed by HPLC to determine the pollutant concentration.

Results and Discussion

Concerning the results obtained for the photodegradation of sulfamethoxazole, the removal efficiency with almost all of the eleven photocatalysts tested reached a value higher than 95% after two hours of treatment under irradiation with a visible light lamp. Similar results have been obtained after 80 minutes of treatment in the case of irradiation with direct sunlight (Figure 1). In the case of atenolol similar results were observed.

Considering that nowadays pollutants of emerging concern are frequently detected in wastewater and aquatic environments worldwide at concentrations ranging from ng/L to µg/L and that they cannot be completely removed in conventional wastewater treatment plants, graphitic carbon nitride possess promising features to be an alternative to common wastewater treatment methods in the next future.

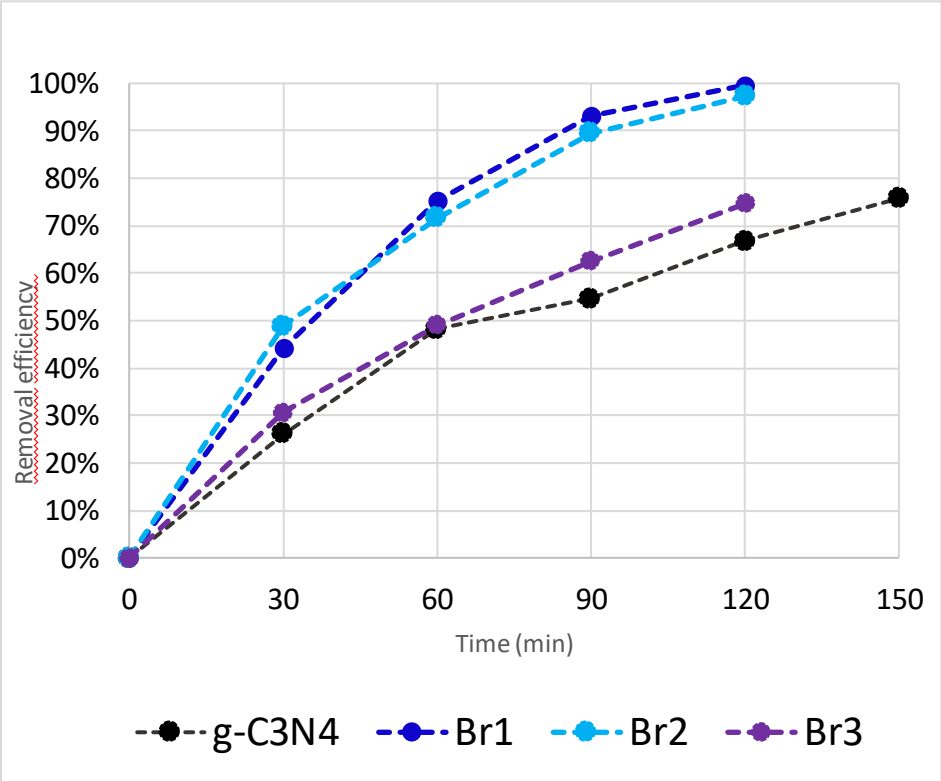


Figure 1 Removal efficiency of four of the produced photocatalysts in the degradation of sulfamethoxazole, under sunlight irradiation.

References

1. S. Patnaik, S. Martha, K. M. Parida, *RSC Advances* **2016**, 46929–46951, 6(52).
2. Y. Li, R. Jin, G. Li, X. Liu, M. Yu, Y. Xing, Z. Shi, *New Journal of Chemistry* **2018**, 6756–6762, 42(9).
3. B. M. Bresolin, P. Sgarbossa, D. W. Bahnemann, *Journal of Environmental Chemical Engineering* **2021**, 106389, 9(6).

Acknowledgements

The authors wish to thank the Department of Industrial Engineering (UniPD – DII) for financing the HYPURE SID2023 project and the Department of Chemical Engineering (DEQ – UC).

Transition metals over C-based materials: unraveling performances and challenges

Sina E. Atakoohi[1], Elena Spennati[1,2], Paola Riani[2,3], Gabriella Garbarino[1,2,*]
[1]*University of Genova, DICCA Dept., Genova, 16145 (Italy)*
[2]*INSTM, UDR Genova, 16146 (Italy)*
[3]*University of Genova, DCCI Dept., Genova, 16146 (Italy)*

** gabriella.garbarino@unige.it*

Significance and Relevance

In the pursuit of carbon neutrality, the conversion of CO_2 to methane or even to syngas will be a pivotal process. This study aims to examine the catalytic performance of cutting-edge carbon-based catalysts, as an alternative to conventional alumina-based ones, in CO_2 hydrogenation and dry reforming reactions. The findings will offer a comprehensive insight into the influence of the support and its impurities on the selectivity of different products.

Preferred and 2nd choice for the topic: Fundamental advances in understanding catalysis, Circular economy
Preferred presentation: *Oral*

Introduction and Motivations

The capture and utilization of CO_2 are regarded as a promising strategy for mitigating the environmental challenges confronting the globe and for achieving carbon neutrality by 2050[1]. In order to reduce CO_2 emissions, in particular those arising from the power sector, the use of hydrogenation reactions to produce CH_4 or CO through Sabatier's or reverse water gas shift (rWGS) reactions appears to be a promising strategy. Furthermore, the production of syngas through dry reforming represents another un-exploited reaction. In general, formulated metal supported catalysts suffer deactivation due to coke deposition and/or particle sintering[2-5], thus hindering the exploitation at the industrial scale. For these reasons, the development of new catalysts is a challenge. Among the potential options, carbon-based materials are well-suited as catalyst supports due to their low cost, natural abundance, high stability in both acidic and basic conditions, and high catalytic activity in several reactions[6-7]. In this study, carbon-based supports, including commercial graphene nanoplatelet (Gnp), homemade Gnp prepared via the molten salt method, and reduced graphene oxide, were employed as a support for Ni, Co, and/or Ru-based catalysts for CO_2 hydrogenation and dry reforming reactions.

Materials and Methods

The catalysts, with a total metal loading of 2 and 5 wt.% for Ni and Co-based ones and 0.5 wt.% for Ru-based ones, were supported on commercial (C) or homemade (H) graphene nanoplatelets (Gnp) and reduced graphene oxide (rGO). They were prepared by incipient wetness impregnation using ethanol as the solvent. The prepared materials were characterized by a range of techniques, including vibrational spectroscopies, XRD, FE-SEM, SEM-EDXS, and TEM. Prior to testing in Sabatier's, rWGS, and dry reforming reactions, an in-situ drying-reducing process was investigated and performed. A novel method for determining carbon loss during drying-reduction tests was developed and performed using online IR spectroscopy.

Results and Discussion

In Figure 1, CO_2 hydrogenation catalytic performances with the prepared catalysts are shown in terms of yield to methane and CO. At all temperatures investigated, the carbon-based catalysts exhibited a higher catalytic performance in rWGS reaction than Sabatier's one. It is noteworthy that the cobalt catalyst exhibited enhanced catalytic activity at low temperatures (T < 632 K), with a CO yield of 38% at 632 K. The Ni and Ru-based catalyst supported on homemade Gnp demonstrated

superior catalytic activity in terms of CO production compared to those supported on commercial ones. Conversely, catalysts supported on rGO demonstrated limited catalytic activity in both reactions. The characterization of exhaust catalysts revealed partial graphitization of Gnp and the presence of distributed Ru- and Ni-based particles (with an average dimension of 5-10 and 10-25 nm, respectively), even though sulfur impurities (0.5 wt%) appears upon in-depth investigations.

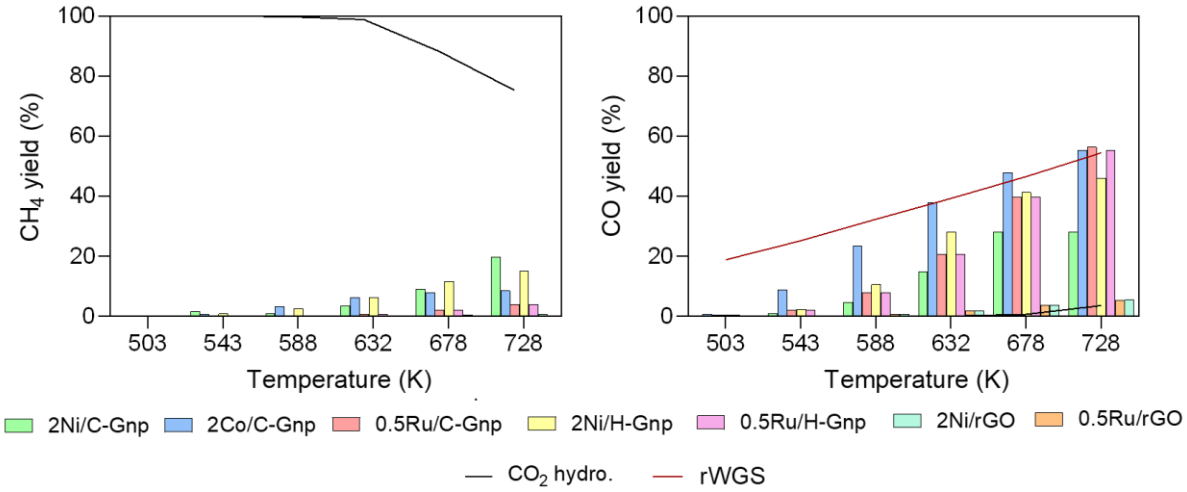


Figure 1. CO_2 hydrogenation catalytic performances with carbon-based catalysts

Co- and Ni-based catalysts showed promising results in dry reforming reaction obtaining a CO yield above 80% in the temperature range 773-973 K and at present time characterization of the exhaust materials is undergoing.

References

1. IEA.org /reports/global-energy-review-2021/CO_2-emissions.
2. G. Garbarino, P. Riani, L. Magistri, G. Busca, *Int. J. Hydrogen En.* **2014**, 39, 11557-11565.
3. G. Garbarino, D. Belotti, P. Riani, L. Magistri, G. Busca, *Int. J. Hydrogen En.* **2015**, 40, 9171-9182
4. G. Garbarino, C. Wang, T. Cavattoni, E. Finocchio, P. Riani, M. Flytzani-Stephanopoulos, G. Busca, *Appl. Catal. B: Environ* **2019**, 248, 286-297.
5. P. Riani, I. Valsamakis, T. Cavattoni, V. Sanchez Escribano, G. Busca, G. Garbarino, *Appl. Catal. B: Environ.* **2021**, 284, 119696.
6. M. B. Gawande, P. Fornasiero, R. Zbořil, *ACS Catal.* **2020**, 10, 2231–2259.
7. J. Wu, T. Sharifi, Y. Gao, T. Zhang, P. M. Ajayan, *Adv. Mater.* **2019**, 31, 1–24.

Acknowledgements

G.G. and E.S. acknowledge the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3—Call for tender No. 1561 of 11.10.2022 of Ministero dell'Università e della Ricerca (MUR); funded by the European Union—NextGenerationEU project title "Network 4 Energy Sustainable Transition—NEST" (project code PE0000021).

Doped-perovskites for the solar-powered photocatalytic valorisation of CO_2

Giulia FORGHIERI[a], Giorgia FERRARO[a], Somayeh TAGHAVI[b], Michela SIGNORETTO[a]*

[a] *Università Ca' Foscari Venezia, Via Torino 155, Venezia*
[b]*Faculty of Chemistry, University of Mazandaran, Babolsar 47416-95447, Iran*

**miky@unive.it*

Significance and Relevance

The design of photo-active materials sensitive to the full solar spectrum would be highly desirable to enable the scaling up of CO_2 valorization through photocatalytic and solar technologies. Doped Ba and Ca titanates were successfully employed for the first time in CO_2 photoreduction using solar light.

Preferred and 2nd choice for the topic: CO2 utilization and recycling; Photocatalysis
Preferred presentation: Oral/Short Oral

Introduction and Motivations

Carbon dioxide is an abundant greenhouse amongst the main contributor to the global warming effect. Different strategies have been proposed to reduce CO_2 concentration in the atmosphere, including the conversion into high value-added products like fuels and chemicals[1].

Photocatalysis, intended in this case as CO_2 photoreduction in presence of water vapor, is an alternative catalytic approach, which exploits solar energy as an abundant, unlimited, renewable energy source to enable carbon dioxide conversion into different solar fuels[2], without requiring additional energy input to make the reaction take place. Perovskites such as barium titanate ($BaTiO_3$) and calcium titanate ($CaTiO_3$) are promising photocatalytic materials which show good photostability, corrosion resistance in aqueous solutions and band gap necessary to obtain all the products of carbon dioxide reduction. However, they absorb UV radiation, which constitutes only 4% of the solar spectrum.

Materials and Methods

$BaTiO_3$ and $CaTiO_3$ perovskites were prepared via hydrothermal synthesis and doped with non-metal dopants. The materials were characterized through FT-IR, DRS, SEM-EDX, TEM, N_2 physisorption, and XRD techniques and then tested for CO_2 photoreduction in a gas phase batch reactor.

Results and Discussion

Bare barium and calcium titanates were not active under solar irradiation. However doped perovskites showed good photoactivity under when irradiated with solar light. Compared to the bare perovskites, doping the materials with heteroatoms, likely led to a narrowing of the band gap, suggesting their acquired activity in the visible region of the spectra. Figure 1 shows the increased absiption ability of two differently doped perovskites compared to the bare materials, BaT and CaT. Doped $CaTiO_3$ showed the best photocatalytic activity reaching a TON up to 1.8 $\mu mol/g_{cat}$ relative to methane production.

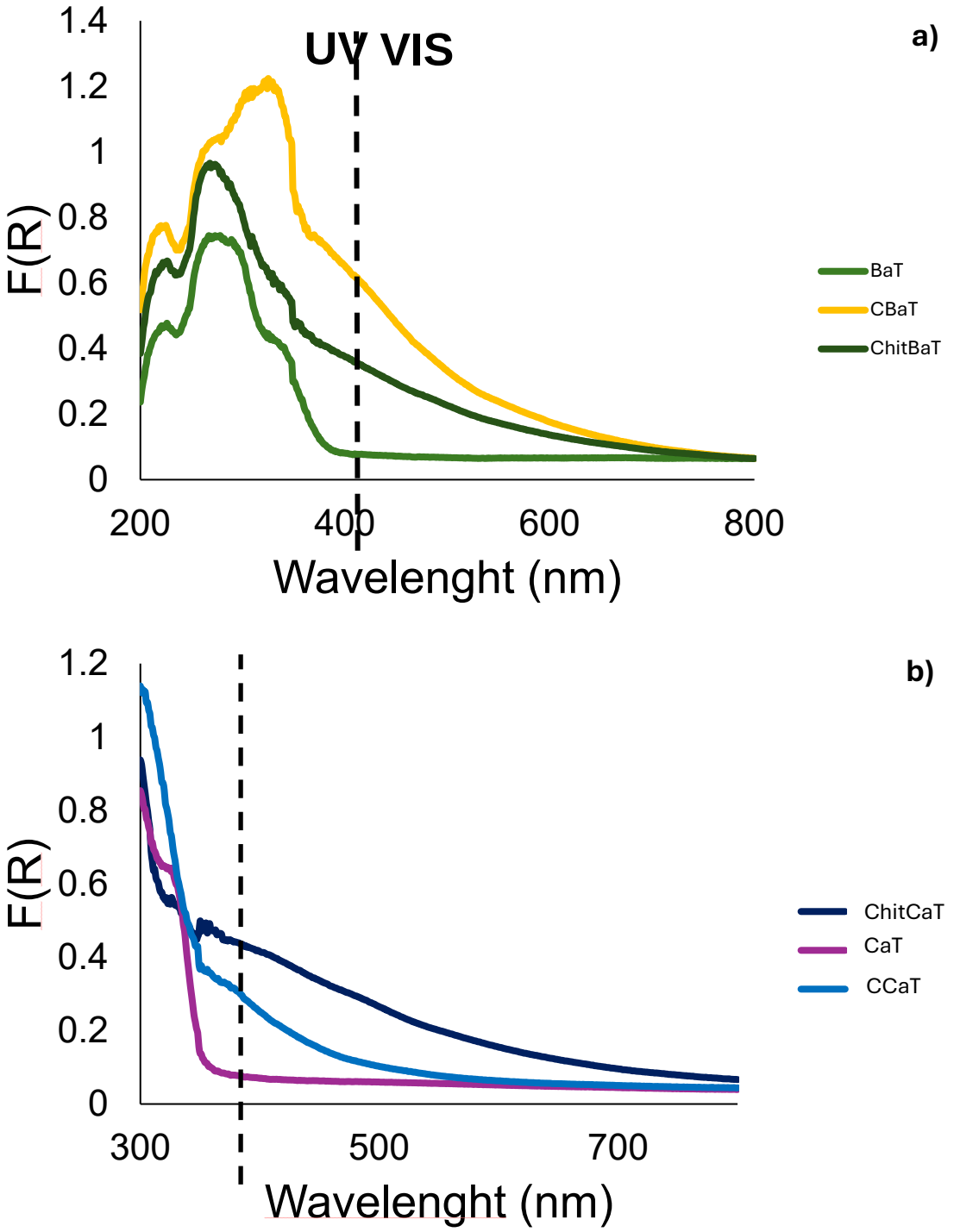


Figure 1 Diffuse reflectance spectra of a) Ba-based and b) Ca-based doped and non-doped materials.

References

1. L. Al-Ghussain, *Environ. Prog. Sustain. Energy*. **2019**, 38, 13-21
2. L. Sun, Y. Wang, N. Guan, and L. Li, *Energy Technol.* **2020**, 8, 1900826

Acknowledgements

The “SCORE2 - Solar-driven COnveRsion of CO2 with HP-HT photorEactor” project is kindly acknowledged for funding.

Cellulose Aqueous Phase Reforming (APR) using Ni and PtNi based catalyst for hydrogen generation: the unexpected effect of reductive atmosphere

Andrea Fasolini[1], Jacopo De Maron[1], Andreas Buono[1], Eleonora Tosi Brandi[1], Francesco Basile[1],

[1]Dept. of Industrial Chemistry "Toso Montanari", University of Bologna, Bologna, Italy
[2]Center for Chemical Catalysis - C3, University of Bologna, Bologna, Italy
** andrea.fasolini2@unibo.it*

Significance and Relevance

This study demonstrates the effectiveness of layered double hydroxide (LDH)-derived catalysts in producing hydrogen from waste cellulose via aqueous phase reforming (APR) with a one-pot approach that minimizes humin formation, enhancing hydrogen yields supporting the development of sustainable energy solutions, contributing to the hydrogen economy and promoting the utilization of wastes for energy generation.

Preferred and 2nd choice for the topic: H2 storage and transportation, Green hydrogen production, energy vectors
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

As part of the hydrogen economy, various processes for producing hydrogen from renewable sources are being explored. One promising method involves the catalytic conversion of waste biomass, particularly cellulose, into hydrogen. Typically, cellulose is converted by hydrolysis to produce an aqueous glucose solution, which can then be subjected to aqueous phase reforming (APR) to yield hydrogen. This catalytic process resembles methane steam reforming and generates hydrogen and carbon monoxide from carbon-based substrates[1,2]. Unlike methane, glucose contains complex structures with C-C and C-O bonds alongside C-H bonds, which facilitates its decomposition and lowers the temperature required for the endothermic reforming reaction (200-250°C). Consequently, APR can be conducted at autogenous pressure within the liquid phase.

$$C_6H_{12}O_6 \rightleftarrows 6CO + 6H_2 \quad \text{Glucose APR}$$

The low-temperature operation enables simultaneous execution of the reforming reaction and the water gas shift (WGS) reaction, which consumes CO produced during reforming and enhances hydrogen yield. However, when glucose is heated above 150°C, it tends to decompose into solid humins[3], which obstructs hydrogen production and blocks catalyst active sites. In this study, we employed a one-pot approach by directly using a cellulose aqueous mixture in APR with a suitable catalyst that possesses both acid-base and redox properties. This method allows for controlled hydrolysis of cellulose, yielding low glucose concentrations that are quickly consumed in the reforming process, thereby preventing humin formation. Tailored catalysts are essential for this approach

Materials and Methods

The LDH-based catalysts were synthesized via coprecipitation and subsequently calcined to form mixed oxides. The final catalysts consisted of Ni^0 supported on MgAl mixed oxide obtained through reduction under H_2. Characterization of the catalysts was performed using XRD, nitrogen physisorption, TEM, TPD, and TPR/OR analyses. An autoclave was charged with cellulose (1.5g), catalyst (0.4g), and water (50.0g) under N_2 or H_2 atmosphere and heated to 250°C. Gas and liquid products were analyzed via GC and HPLC respectively.

Results and Discussion

The Ni^0/Mg(Al)O catalysts exhibited both redox and acid-base functionalities necessary for catalyzing hydrolysis and reforming reactions as well as retro-aldol reactions. In glucose APR experiments,

minimal hydrogen production was observed due to humin formation; however, a significant hydrogen yield (>20%) was achieved using cellulose. This demonstrates the benefits of a one-pot process that integrates hydrolysis with APR. The effect of Ni content on hydrogen yield was also assessed; initially increasing Ni content enhanced yield but resulted in decreased yield at higher concentrations due to larger Ni particle formation reducing the overall metallic surface area. The study also focused on identifying liquid products and their corresponding reaction pathways—an area often overlooked in existing literature. Notably, glucose was not detected in the liquid phase, indicating its rapid consumption by APR compared to its generation from cellulose hydrolysis. Among the identified products were lactic acid, acetic acid, and ethylene glycol; the latter likely serves as an intermediate for hydrogen production due to its ease of reforming. Adding Pt to the NiMgAl catalyst facilitated a reduction in the temperature required for reduction (as indicated by TPR), thereby enhancing both the reforming reactions and C-C bond cleavage, which increased the hydrogen yield to 40%. The highest yield, exceeding 50%, was achieved in a hydrogen atmosphere, which accelerated the hydrolysis rate and promoted rapid reforming due to the NiPt active phase. The influence of reaction time was investigated to propose a reaction mechanism, while varying reduction temperatures helped identify the optimal reduction procedure. Additionally, Pt was impregnated onto a commercial support, demonstrating the superior performance of the catalyst developed in this study and the reaction mechanism was drawn starting from the obtained results.

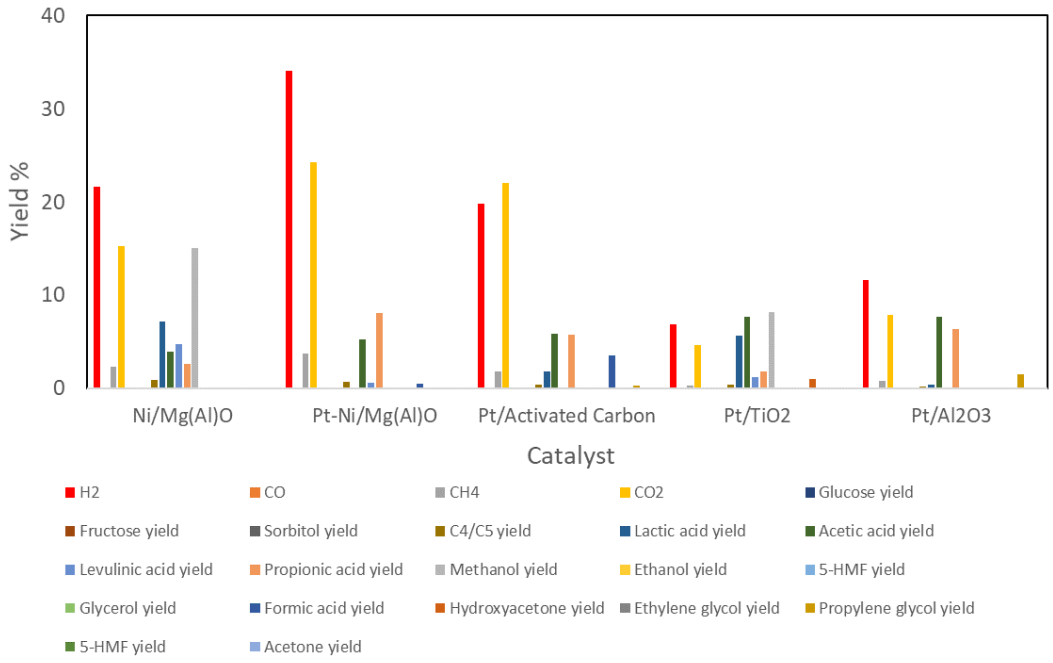


Figure 1. Gas and liquid phase products obtained over different Pt-based catalyst at 250°C for 3 h.

References

1. A. Fasolini et al., *Catalysts* **2019,** *9.9, 722*.
2. A. Fasolini et al., *Catalysts* **2019,** *9.11, 917*
3. S. Taghavi et al. *Catalysts* **2020,** *8.7, 843*

TiO_2 or Nb_2O_5 composites with graphene or graphene oxide as photocatalysts for Photoreforming of organics to obtain H_2

Alberta GENCO[1,2*], Elisa I. García-López[3], Narimene Aoun[1], Bartolo Megna[1], Conchi O. Ania[4] , Giuseppe Marcì[1]

[1]*Department of Engineering (DI), Viale delle Scienze, University of Palermo, Palermo, Italy*
[2]*Department of Chemistry, University of Perugia, Perugia, Italy*
[3]*Department of Chemistry (STEBICEF) University of Palermo, Italy*
[4]*POR2E Group, CEMHTI CNRS (UPR 3079), Université d'Orléans, 45071 Orléans, France*

**alberta.genco@dottorandi.unipg.it*

Significance and Relevance

The conversion of solar energy into other energy vectors is a promising approach to address the challenges of global sustainability. The production of H_2 from sunlight represents an attractive alternative to the use of fossil fuels to meet current energy demands. In this study, photoreforming reaction in the presence of aqueous solutions of ethanol, glycerol or microplastics (polyethylene terephthalate or polylactic acid) aqueous dispersions and of a semiconductor irradiated under UV or natural solar light were performed to obtain H_2. The heterogeneous photocatalysts used consisted of an oxide (Nb_2O_5 or TiO_2) forming a composite with a carbon-based material such as graphene (G) or graphene oxide (GO).

Preferred presentation: Oral

Introduction and Motivations

The photoreforming of aqueous solutions containing organic compounds integrates the photocatalytic splitting of water with the oxidation of organic substances into a single process under ambient conditions. In this technology a semiconductor, excited by suitable energy, generates electron/hole pairs allowing redox reactions; i.e. protons are reduced by the electrons to obtain H_2 and an organic molecule acts as a hole scavenger resulting in the production of a partially oxidized derivatives. Previous investigations showed that Nb_2O_5 can act as an excellent catalyst with activity comparable to that of TiO_2, which is one the most used photocatalyst for H_2 production[1]. Both TiO_2 and Nb_2O_5 suffer from rapid recombination of charge carriers and low solar-energy utilization, due to their large bandgap. Various strategies to make them active under sunlight and to enhance their photocatalytic activity have been explored, including the combination of these semiconductors with carbon materials such as graphene (G) or graphene oxide (GO).

This research focuses on the development of composite photocatalysts that realize heterostructures obtained by varying the amount of carbon material (ranging from 5% to 20%) relative to the mass of the oxide semiconductor (TiO_2 or Nb_2O_5) for the photoreforming of organic compounds dissolved in water[2]. In these composites, the oxide semiconductor acts as the photocatalyst, while graphene and graphene oxide play the role of electron reservoirs and carriers, facilitating electron transfer to the reaction sites. Photoreforming tests were performed using as hole scavengers ethanol or glycerol by irradiating the solid under UV or natural sunlight. Selected experiments using microplastics as scavengers were also conducted to explore their possible degradation considering the continuous and worrying expansion of this type of residue in aquatic environments and its devastating effects on ecosystems and human health.

Materials and Methods

Nb_2O_5 was synthesized through a hydrothermal process using Ammonium Niobium Oxalate as precursor whereas TiO_2 was commercial Evonik P25. The composites with Graphene were prepared by sonication of G (commercial Graphene-XT) and the semiconductor in CH_3CN. The amount of G with respect to the oxide ranged from 5 to 20 % w/w. The samples were labelled Ti-G or Nb-G, followed by the mass of G per 10 g of semiconductor, i.e. Ti-G-10:0.5; 10:1 or 10:2. Graphene Oxide was prepared using Hummer's method[3] and the composites oxide-GO were prepared in a 10:1 mass ratio and labelled as Ti-GO-10:1 or Nb-GO -10:1.

Photoreforming tests were performed in a 50 mL cylindrical Pyrex photoreactor with 35 mL of aqueous solution of ethanol, glycerol, PET or PLA, 0.32 $g \cdot L^{-1}$ of photocatalyst. In the current investigation experiments were carried out in the absence and in the presence of Pt corresponding to 1% Pt w/w relative to the total mass of catalyst[4]. The photocatalytic activity of the materials was evaluated under UV LED or natural sunlight irradiation.

Results and Discussion

The histograms in Figure 1 show the H_2 productivity (moles of H_2 formed per gram of catalyst and per hour of irradiation) under UV LED irradiation of photocatalysts in the presence of Pt using different substrates. TiO_2-based photocatalysts were more active than those of Nb_2O_5. In general, better results were obtained with heterostructures Ti-G 10:1 and Ti-GO 10:1. The photoreforming of ethanol Fig. 1(A) gave rise to the best performance, particularly in the presence of Ti-G 10:1, which evidenced a better performance than the corresponding pristine TiO_2. The results reported in Fig 1(C) are significantly lower when compared to Figs 1(A) and 1(B), demonstrating how ethanol and glycerol, due to their simpler structure, can be easily oxidized with respect to microplastics, which have high structure complexity.

The highest performance was achieved with Ti-G 10:1 in the presence of Pt using ethanol. In these conditions, the productivity was of 311 $mmol \cdot h^{-1} \cdot g^{-1}$ with an apparent quantum efficiency (AQE) of 100% under UV light and 13 $mmol \cdot h^{-1} \cdot g^{-1}$ with AQE 18% under natural sunlight irradiation.

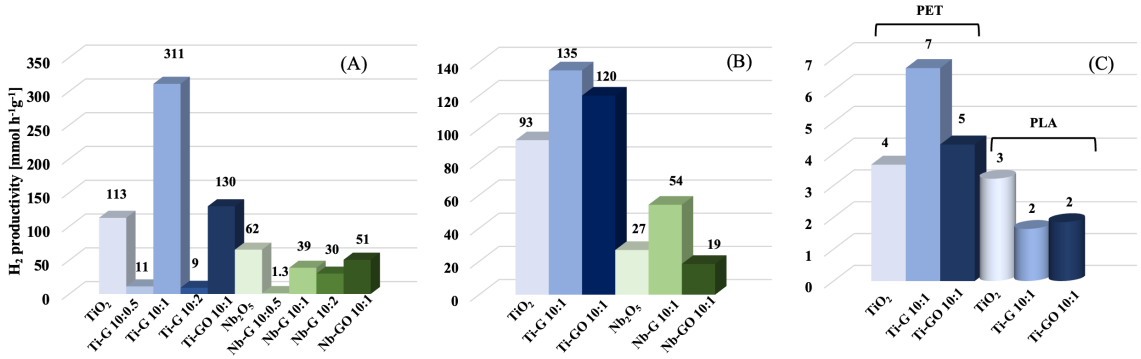


Figure 1 H_2 productivity under UV irradiation in the presence of (A) ethanol (B) glycerol and (C) PET and PLA

References

1. E.I. García-López, E.I.; Genco, A.; Lagostina, V.; Paganini, M.C.; Marcì, G. *Catal. Today*, **2023**, 423, 114283.
2. H. Kim, G. Moon, D. Monllor-Satoca, Y. Park, W. Choi, *The J. of Physical Chemistry C* **2012** *116* (1), 1535-1543.
3. W.S. Hummers Jr, R.E. Offeman, Preparation of Graphene Oxide, **1957**.
4. E.I. García-López, P. Lo Meo, A. Di Vincenzo, L. Palmisano, G. Marcì, Catal. Today, **2023**, 413-415 113965.

Revealing the effect of Pd on Co-based catalysts in dry and bi-reforming of methane

Kuralay T. TILEGEN[1, 2], Sholpan S. ITKULOVA[*1,2], Yerzhan A. BOLEUBAYEV[1], Aidana K. AITZHANOVA[1], Makpal A. ZHUMASH[1]
[1]D.V. Sokolsky Institute of Fuel, Catalysis, and Electrochemistry, 142, Kunaev str., Almaty, 050010, Kazakhstan
[2]Kazakh British Technical University, 59, Tole bi str., Almaty, 050000, Kazakhstan
* s.itkulova@kbtu.kz, sholpan.itkulova@gmail.com

Significance and Relevance

The modification of Co-based catalysts with a small amount of Pd (0.05-0.1 wt. %) significantly improves the performance of catalysts in dry and bi-reforming of methane (DRM, BRM) in terms of high activity and stability. The conversion degree of feed gases (CH_4, CO_2) varied within 61-99% for DRM and BRM depending on temperature, feed composition, amount of Pd dopant, and method of preparation. The addition of water to feedstock for DRM increases the methane conversion and the H_2/CO ratio in produced syngas.

Preferred and 2nd choice for the topic: ……..
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The dry and bi-reforming of methane can be considered as a promising technology to realize a low-carbon economy by utilizing greenhouse gases (CH_4, CO_2) and directly generating synthesis gas with a balanced ratio of H2 and CO for high-value chemicals. The biggest stumbling blocks for the large-scale industrial application of these processes are the catalysts' coke formation and stability problems. Adding noble metals as promoters to the catalysts substantially increases the catalyst's resistance to carbon deposition and their durability without loss in activity[1, 2]. This work's main objective is to study Pd's promotional effects on Co-based catalysts with a small content of Pd during dry and bi-reforming of methane.

Materials and Methods

The bimetallic Co-Pd catalysts were prepared by wet co-impregnation and sol-gel methods. The alumina was co-impregnated with Co and Pd-based precursors. For the preparation of catalysts by sol-gel (modified Pechini method), citric acid was used as a gelling agent. The performance of catalysts was studied in DRM and BRM at an equimolar feed ratio of CH_4:CO_2. The 5%Co-Pd/Al_2O_3 catalysts were characterized by XRD analysis, TPR-H_2, SEM, TEM, and BET.

Results and Discussion

Since DRM is a highly endothermic process the effect of temperature is significant. As shown in Figure 1, increasing the temperature leads to higher conversion degree of methane and greater product yields, exceeding 92% and 14 µmol/(g·s), respectively. When 20 vol.% steam is introduced to the DRM process using a 5%(Co-Pd(99:1))/Al_2O_3 catalyst, the H_2/CO ratio increases from 1.01 to 1.34. Furthermore, this yields substantial amounts of hydrogen and carbon monoxide. This indicates that varying the steam volume in the feed allows the production of synthesis gas with desirable ratios of H_2/CO, making it suitable for further applications, such as Fischer-Tropsch synthesis. The bimetallic Co-Pd catalysts demonstrate exceptional effectiveness, largely due to the synergistic interactions between cobalt and palladium, which enhance the dispersion and reducibility of cobalt. Even minimal quantities of palladium (ranging from 0.05-0.1 wt. %) significantly influence cobalt's performance, maintaining high activity and selectivity over a long time, which confirmed by stability test for 100 hours.

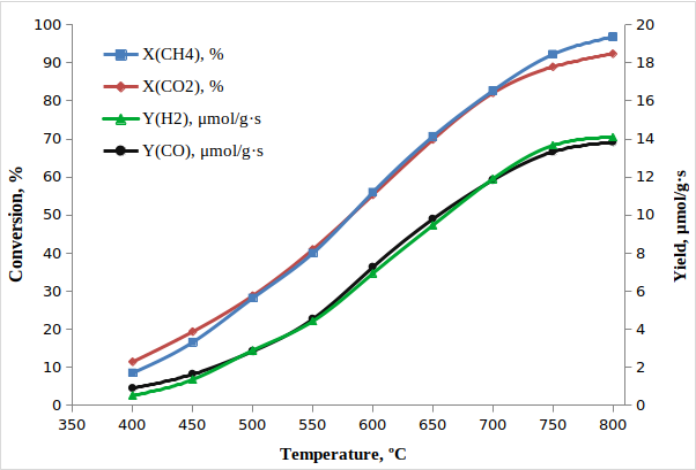


Figure 1 The dependence of reactant's conversion (CH_4, CO_2) and yield of products (H_2, CO) on temperature in DRM over 5%(Co-Pd(99:1))/Al_2O_3 at CH_4:CO_2(1:1), P=1 atm, GHSV=1000h^{-1}

References

1. W. Jang, J. Shim, H. Kim, S. Yoo, H. Roh, *Catalysis Today* **2019**, *324*, 15–26.
2. S. Bhattar, Md. Abedin, S. Kanitkar, J. Spivey, *Catalysis Today* **2021**, *365*, 2–23.

Acknowledgements

The authors wish to thank the Ministry of Education and Science of the Republic of Kazakhstan for funding this research (Grant No AP19679439).

Hydrogen production by chemical looping methane pyrolysis

Luca Consentino[1,2], Francesca Deganello[2], Rut Guil-Lopez[3], Valeria La Parola[2*], Leonarda Francesca Liotta[2], Giuseppe Pantaleo[2]

[1] *Department of Biological, Chemical and Pharmaceutical Sciences and Technologies (STEBICEF), University of Palermo, V.le delle Scienze Ed. 17, 90128 Palermo, Italy;* [2] *Institute for NanoStructured Materials, Italian National Research Council (ISMN-CNR), Via Ugo La Malfa 153, 90146 Palermo, Italy,* [3] *Instituto de Catálisis y Petroleoquímica, Spanish National Research Council (ICP-CSIC), 28049 Madrid, Spain*

[*] *valeria.laparola@cnr.it*

Significance and Relevance

Chemical looping reforming of methane turned out to be a promising process to produce pure hydrogen via catalytic methane pyrolysis overcoming the problem of the building up of carbon on catalyst surface. In addition, pure CO can be produced by using CO_2 as an oxidant in the oxidation step. Among the studied catalysts, **NiAlCa** mixed oxide, prepared by thermal decomposition of like-hydrotalcite material, showed the best performance and stability.

Preferred and 2nd choice for the topic: H2 storage and transportation, green H2 production, hydrogen vectors; Sustainable and clean energy production and transport.
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster) Oral preferred

Introduction and Motivations

The concomitant increase in energy use and CO_2 emission in the atmosphere is of major concern for the environmental equilibrium and earth health of the next future.

Hydrogen is an energy vector with attractive attributes, such as lightness, storability, reactivity, high energy content per unit mass, and easy production at industrial scale. Furthermore, hydrogen can be used without direct emissions of air pollutants or greenhouse gases and can be produced from a diverse range of low-carbon energy sources. Chemical looping technologies can be applied as a valuable approach for hydrogen production, due to the high energy efficiency and inherent CO_2 capture ability[1]. This study concerns the investigation of three types of nickel-based materials active in the decomposition of methane for hydrogen production used in the first step (reduction step) of the chemical looping, followed by a second step (oxidation step) in either Air (CL_AIR) or CO_2 (CL_CO2) for the removal of the carbon accumulated during the reduction step.

Materials and Methods

Three catalysts with Nickel in different environments were prepared: Ni coprecipitated with cerium oxide (**NiCe**), Ni in a **NiAlCa** mixed oxide prepared by thermal decomposition of like-hydrotalcite material, and Ni in **$LaNi_{0.8}Co_{0.2}O_3$** perovskites structure. All samples were characterized by X-ray diffraction (XRD), nitrogen physisorption, temperature programmed reduction (TPR) with diluted H_2 or CH_4 and temperature programmed oxidation (TPO) techniques. Redox stability was checked with multiple REDOX cycles and chemical looping experiments were carried out isothermally, alternating the gas composition every 10 minutes from 15 vol% of CH_4 in N_2 to air or CO_2. The reaction temperature was chosen for each sample based on temperature programmed reduction measurements with methane.

Results and Discussion

The different nickel environments of the three catalysts have been confirmed by XRD and TPR measurements. The redox stability, analyzed by multiple TPR-TPO cycles, indicated that $LaNi_{0.8}Co_{0.2}O_3$ is the most stable material . Both NiCecp and NiCaAl (exHT) modify their profile after the first TPR-TPO cycle by stabilizing the Ni phase. CH_4-TPR allowed us to identify the best temperature of methane decomposition for each material: 680°C for $LaNi_{0.8}Co_{0.2}O_3$, and 600°C for NiCecp and NiCaAl (exHT).

Figure 1 shows two cycles of CL-AIR (lower panel) and CL-CO_2 (upper panel) for the three materials. The catalytic activity for hydrogen production follows the order NiCaAl (exHT)> NiCe (cp)> $LaNi_{0.8}Co_{0.2}O_3$ with all three catalysts showing good stability as evidenced by the hydrogen production after ten cycles. Interestingly the oxidation step (AIR or CO_2) influenced the nature of the active phase and its interaction with the support/matrix. In the case of $LaNi_{0.8}Co_{0.2}O_3$ and NiCe(cp) the repeated reoxidation in CO_2 produced Ni active phase less effective in the activation of methane, essential step for the catalytic methane pyrolysis. On the contrary, NiCaAl(exHT) shows analogous performances both using air and CO_2 as oxidizing agent.

In conclusion, NiCaAl(exHT) is a promising material with good activity and stability for hydrogen production via methane pyrolysis. Its activity in hydrogen production via chemical looping processes is worth of further study to optimize the experimental details for a scale up study.

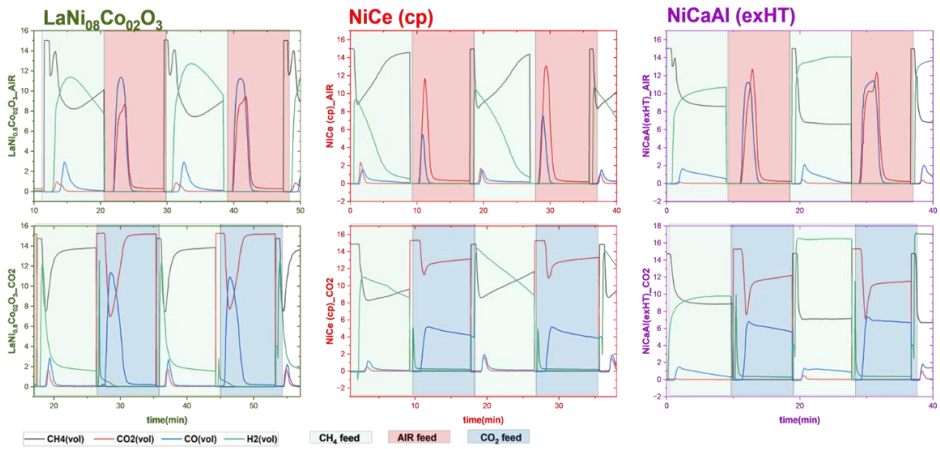


Figure 1 CH_4, CO and CO_2 concentration (ppm) during chemical looping cycle: CL_AIR (upper panel) and CL_CO_2 (lower panel). Enlargement of two cycles.

References

1. Li, L.; Tang, D.; Zheng, Z.; Zhao, C. Catalysts **2018**, 8, 257-269.

Acknowledgements

Project NAUSICA (PON "R&S 2014-2020", grant n. ARS01_00334), Short Term Mobility (STM) 2022 CNR

Biomass-derived Activated Carbon for H_2 storage: influence of solvent and doping agent on the adsorption properties

Alessia MARINO[1], Carlo POSELLE BONAVENTURA[2], Sara SCIARRETTA[1], Giuseppe CONTE[2], Alfredo ALOISE[1], Chiara PELOSI[3], Andrea LAZZARINI[1], Celia DUCE[3], Luca BERNAZZANI[3], Alfonso POLICICCHIO[2], Marcello CRUCIANELLI[1]

[1] *University of L'Aquila, Department of Physical and Chemical Sciences, via Vetoio, 67100, L'Aquila, Italy.*
[2] *University of Calabria, Physics Department, Via Bucci, 87036, Rende, Cosenza, Italy.*
[3] *University of Pisa, Department of Chemistry and industrial chemistry, Via Moruzzi, 56124, Pisa, Italy.*
alessia.marino3@univaq.it

Significance and Relevance

Hydrogen represents a suitable alternative to fossil fuels, but efficient storage is still challenging. Biomass-derived carbons, enhanced by heteroatom doping, offer a promising solution. This work investigates boron-doped activated carbons for H_2 storage, by evaluating the impact of solvents and reaction conditions on textural properties and adsorption performance. Results show that both reaction time and solvent type affect surface area, and then the hydrogen adsorption, indicating that the presence of boron can improve H_2 uptake at 77 K, while harsh reaction conditions may cause a structural collapse.

Preferred and 2nd choice for the topic: "H_2 storage and transportation, green H_2 production, hydrogen vectors", and "Sustainable and clean energy production and transport"
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

In the view of reaching the carbon neutrality, new solutions for energy production and transportation are matter of studies from the scientific community. In this context, hydrogen represents one of the most promising clean and sustainable alternative to fossil fuels. However, the limiting factor still lies in its storage, since it requires both an efficient adsorption and a highly reversible release under mild conditions. Biomass-derived carbons represent a class of efficient and low-cost materials suitable to this purpose, which can be further upgraded by adjusting textural properties, as well as by inserting heteroatoms as dopant [1]. In this work, the influence of boron as activated carbon-dopant on the H_2 adsorption-desorption properties has been studied [2]. To this aim, the role of different solvents and times, generally used in boronation reactions, was also investigated, in order to correlate the change in the textural properties and the actual contribution of the selected heteroatom [3].

Materials and Methods

Coconut-derived activated carbon was added to the selected solvent and then the mixture was kept under stirring for designated times (3, 7, or 10 days) at 80 °C. The solid was then separated by centrifugation and dried. The solvent-carbon matrix interaction has been investigated for the following solvents: tetrahydrofuran, N-metyl-2-pyrrolidone, 1,2-dimethoxyethane, toluene, deionized water, ethanol, and isopropyl alcohol. A similar procedure was used for boron doping, by adding to the mixture different concentrations of BH_3 (8 and 17 mmol/g). The obtained samples were characterised by N_2-physisorption, TGA-IR, Raman and IR spectroscopy, and SEM. The H_2 storage performance was evaluated at low pressure (up to 1 bar).

Results and Discussion

The solvents screening has evidenced a general change in the textural and morphological (**Figure 1**) properties of the activated carbon, as a function of both solvent type and reaction time, regardless the presence of the doping agent.

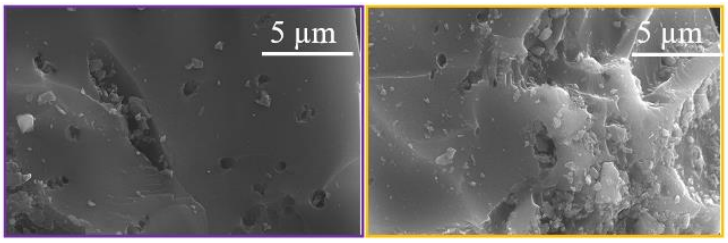


Figure 1 – SEM images of parent activated carbon (left, purple) and after treatment in THF for 10 days (right, yellow).

In particular, NMP_7d and TOL_3d showed the highest surface area decrease, while just a small modification was observed in THF_3d, compared to the parent carbon. As expected, these results reflect on H_2 storage performance, showing that the adsorption is strictly related to the available surface area. When boron was used as doping agent, two different effects were observed as a function of borane concentration and reaction time. In particular, the H_2 uptake increased according to the reaction time when the lowest concentration of BH_3 was used, while by doubling the amount of B the opposite trend was observed (**Figure 2**). Lastly, both the highest concentrations of dopant boron and times led to a collapse of the activated carbon framework.

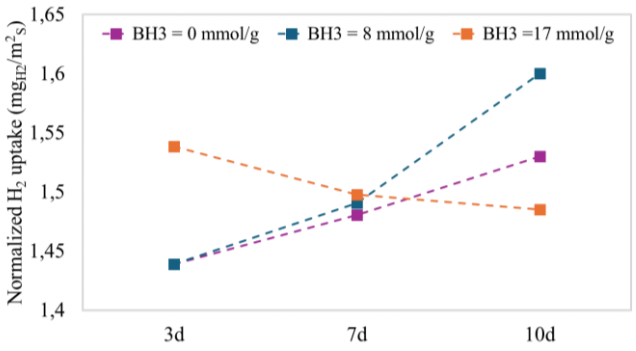


Figure 2 – Normalized H_2 uptake vs time and BH_3 concentration.

The obtained results revealed an active role of solvent and reaction time on the activated carbons framework modification, which impacts the H_2 storage performance. However, the presence of B can improve H_2 adsorption-desorption properties, despite the solvent-related effects, demonstrating the high potential of these doped biomass-derived carbons in H_2 storage application.

References

1. A. Lazzarini et al., *Compounds*, **2023**, 3(1).
2. A. Marino et al., "Evaluation of solvent role in biomass-derived activated carbon functionalization for H_2 storage", in preparation.
3. A. Marino et al., "Boronation of biomass-derived activated carbon for H_2 storage application", in preparation.

Synthesis of Nano-Sil1/TiO_2NTs Composite photocatalyst

Rosalba PASSALACQUA*[1], Alfredo ALOISE[2], Alessia MARINO[2], Nicola DI NICOLA[2], Siglinda PERATHONER[1], Gabriele CENTI[1]

[1] *University of Messina, Department of Chemical, Biological, Pharmaceutical and Environmental Sciences (ChiBioFarAm) & INSTM CASPE (Lab. of Catalysis for Sustainable Production & Energy), Viale F. Stagno d'Alcontres 31, 98166 Messina, Italy*
[2] *Department of Physical and Chemical Sciences, University of L'Aquila, via Vetoio, Coppito 2 67100 L'Aquila, Italy*

** rpassalacqua@unime.it*

Significance and Relevance

In this work, we report the preparation of a ZSM-5/TiO_2NTs composite obtained using an innovative synthesis approach in which nanocrystals of Silicalite-1 zeolite were growth directly on TiO_2 nanotubes[1] by modified Steam Assisted Crystallisation (SAC)[2], leading to the incorporation of the zeolite inside the titania nanotube's structure. The resulting material was denoted as nano-Sil1/TiO_2NTs.

The synthesized material represents a promising new heterogeneous catalyst in which selectivity can be modulated by modifying the properties of the nanozeolite confined in a well-ordered structure having a controlled geometry, like titania nanotubes.

- *Preferred and 2nd choice for the topic: Photocatalysis and photoelectrocatalytic approaches, solar energy utilization / Green chemistry and biomass transformation, renewable resources conversion / Water treatment*

Preferred presentation: Short Oral

Introduction and Motivations

TiO_2 in its anatase form is one of the most widely used photocatalytic active material, due to its high stability and low cost. In this approach, typically anatase nanocrystallites in tubular form are decorated with zeolites. The potential advantage of using TiO_2 nanotubes as a substrate for zeolites is that a very defined geometry for the photocatalytic decomposition can be established.[3] The aim is to combine the excellent photocatalytic functionality of the TiO_2 nanotubes with the selective capturing ability of zeolites to produce a new generation of 'trapping' photocatalyst. The resulting composite coupling the photocatalyst properties of titania with the decomposition ability for organics of zeolites can be used for traditional purpose like pollutant removal from wastewater or for the abatement of VOCs in gaseous effluents[4] thanks to the outstanding adsorbent capability of zeolite, but also for reactions of industrial interest (biomass conversion) exploiting the specific nature of the zeolite counterpart.

Materials and Methods

A novel two-steps coating technique was used for composite preparation. Firstly, in a dip-coating step a zeolite synthesis gel, typically consisting of a source of silica (tetraethylortosilicate, TEOS), a templating agent (tetrapropylammonium hydroxide, TPAOH), and water was homogeneously dispersed on top of a TiO_2 substrate. A hydrothermal synthesis was then carried out. For the coating step the so treated substrate was transferred into a supported-Teflon covered steel autoclave, then heated up to 170 °C and the temperature was kept for 24 hours. This process facilitates the crystallization of the Silicalite-1 on the walls of the titanium nanotubes without affecting (clogging) the tubular structure.

The organic template was then removed, without affecting the anatase titania phase, by a following step involving the calcination of the composite in static air at 450 °C for 8 hours.

Results and Discussion

The obtained composite was characterized by XRD, SEM, TEM, and N_2 physisorption[3], to evaluate the physicochemical and structural properties, as well as the nanocrystals distribution on titania nanotubes.

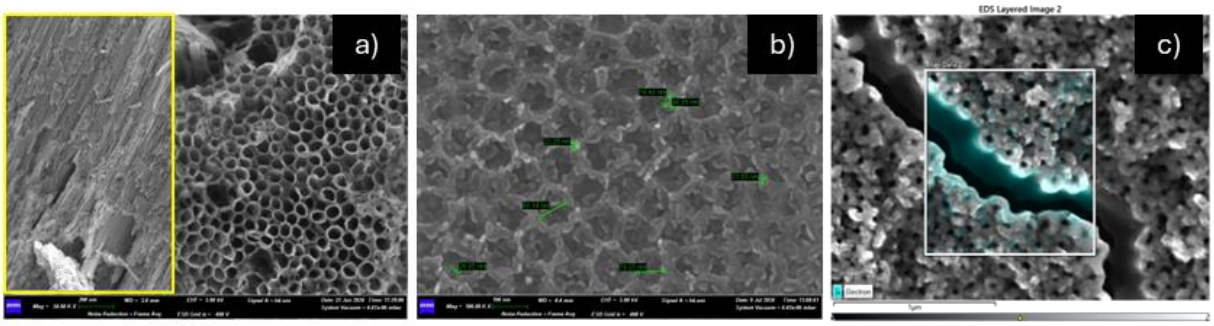


Figure 1. *a) SEM images of the top view and, in the yellow insert on the left, of the cross-section view of the TiO_2 nanotubes before SAC. b) SEM image of the prepared composite: nano-Sil1/TiO_2NTs showing the incorporation of the zeolite inside the titania nanotube's structure. c) EDS layered image of the sample post synthesis not calcined highlighting the presence of Si in light blue.*

The composite is under consideration for further testing in reactions of industrial interest.

References

1. R. Passalacqua, S. Perathoner, G. Centi, *Catalysis Today* **2015**, 251, 121.
2. H. Yang, P. Yang, X. Liu, Y. Wang, *Chemical Engineering Journal* **2016**, 299, 112.
3. I. Paramasivam, A. Avhale, A. Inayat, A. Bösmann, P. Schmuki, and W. Schwieger, *Nanotechnology*, **2009**, 20, 225607.
4. J. Fernández-Catalá, M. Sánchez-Rubio, M. Navlani-García, Á. Berenguer-Murcia, and D. Cazorla-Amorós, *ACS Omega* **2020**, 5(48), 31323.

Modified Montmorillonite-based catalysts for the photothermo-catalytic reduction of CO_2 into solar fuels

Giusy DATIVO*[,1], Salvatore SCIRÈ[1], Giuseppe COMPAGNINI[1], Roberto FIORENZA[1]
[1]*University of Catania, Dep. of Chemical Sciences, Viale Andrea Doria 6, Catania, Italy.*
** giusy.dativo@phd.unict.it*

Significance and Relevance

The structural modification of Montmorillonite K30 with the intercalation of Ni and Ce ions and the subsequent coating with mixed Mn and Cu metal oxides allowed to obtain a performing and green catalyst used for the photothermo-catalytic CO_2 conversion into solar fuels (CO and CH_4).

Preferred and 2nd choice for the topic: (1) Photocatalysis and photoelectrocatalytic approaches, solar energy utilization /(2) CO_2 utilization and recycling.
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The CCU (carbon capture and utilization) permits to mitigate the impact of carbon dioxide, the main greenhouse gas, and to overcome the use of fossil fuels thanks to its valorization towards the conversion into solar fuels[1]. In this work the reduction of CO_2 led to CO and CH_4 using a hybrid catalytic approach as the photothermo-catalysis[2], and unconventional and not critical photocatalysts, as the composites formed between montmorillonite K30 and Mn-Cu mixed oxides.

Materials and Methods

The modification of K30 with Ni and Ce was made at first, activating the Montmorillonite with acetone and after adding the corresponding Ni and Ce nitrate precursors. The obtained slurry was then treated with a hydrothermal method. The coatings with Mn and Cu oxides were done on the as-obtained K30-Ni/Ce with precipitation method using KOH 1M. The catalytic tests were conducted at 120°C in a cylindrical batch reactor using a solar lamp and irradiating for 5h. The analysis of the reaction products was carried out by GC-TCD/FID. The structure and the morphology of the as-synthesized catalysts was investigated by SEM and FT-IR, while the optical band gap was evaluated by UV-DRS. The catalysts were also characterized by Raman, H_2-TPR, CO_2-TPD and N_2- physisorption measurements.

Results and Discussion

The best performance was obtained by K30-Ni/Ce@$MnCuO_x$ with a 77% of CO_2 conversion and 13.9 and 4.9 mmol/gcat•h (figure 1) of formed CO and CH_4, respectively. For this sample stability tests were also conducted using a H_2 flow for the reduction of the fresh sample and for its re-activation (figure 2). Indeed, after a deactivation of 10% in the third run (each run is a photothermal test of 5h), in the subsequent run the sample was reactivated by the H_2 flow, reaching the same photothermo-catalytic activity of the first run after additional 10 h of solar photothermal conditions (figure 2). These results show that the coating using non-critical mixed metal oxides improves the performance of the K30 modified with Ni and Ce. The photothermo-catalysis also represents a greener strategy to mitigate and to valorize the CO_2 impact. Finally, the performance of this modified clay was compared with the new class of "artificial clays" as MXenes prepared using as precursor a MAX phase of Ti_3AlC_2. The MXenes were also modified with Silica, Titania and Ceria to improve photocatalytic and thermocatalytic activity.

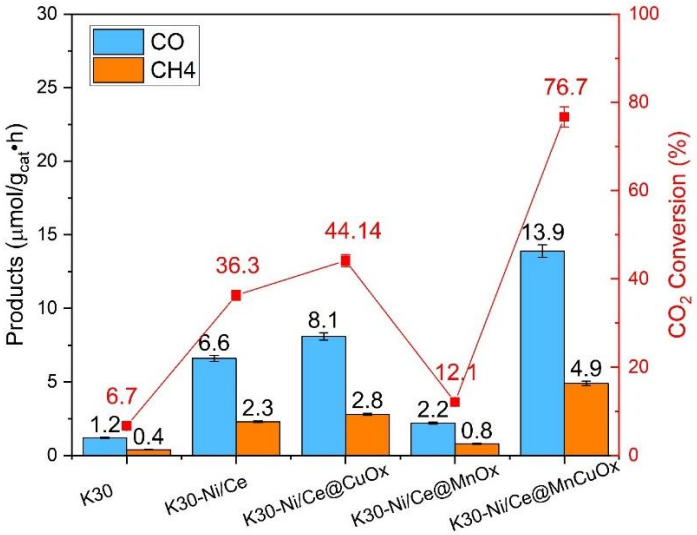


Figure 1 Solar photothermo-catalytic CO_2 reduction at T = 120 ◦C after 5 h of simulated solar irradiation.

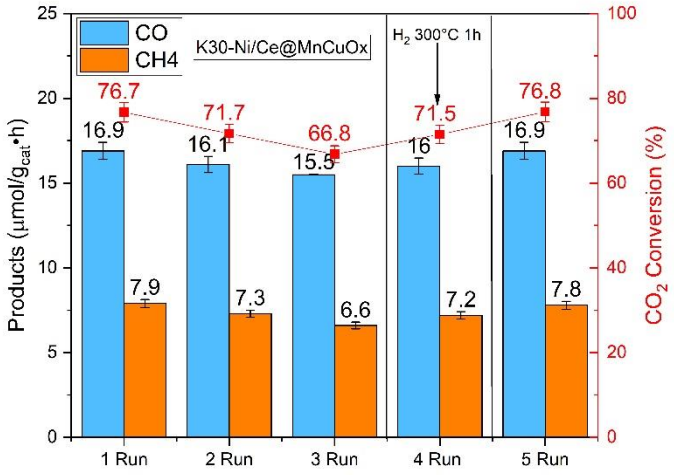


Figure 2 Stability test for the K30-Ni/Ce@$MnCuO_x$ in the solar photothermo-catalytic CO_2 reduction at T=120◦C.

References

1. G. Dativo, E. La Greca, L.F. Liotta, V. La Parola, M. Condorelli, G. Impellizzeri, G. Compagnini, S. Sciré, R. Fiorenza, *Journal of CO2 Utilization* **2024,** 82.
2. R. Ma, J. Sun, D.H. Li, J.J. Wei, *International Journal of Hydrogen Energy* **2020**, *45*, 30288-30324

Acknowledgements

This work was funded by Sicilian Micro and Nano Technology Research and Innovation Center (SAMOTHRACE) CUP-E63C22000900006. R.F. thanks the CO2@photothermocat project funded by MUR (PRIN 2022 PNRR CUP E53D23015700001).

Theoretical insights on innovative solutions for CO2RR with Fe-based single atom catalysts

Giuseppe Santoriello[1], Ida Ritacco[1], Giulia Tuci[2], Giuliano Giambastiani[3], Claudio Ampelli[4], Siglinda Perathoner[4], Gabriele Centi[4], Matteo Farnesi Camellone[5], Lucia Caporaso[1].

[1] *Dept. Chemistry and Biology, University of Salerno, via G. Paolo II 132, 84084, Fisciano (SA), Italy.*

[2] *Institute of Chemistry of OrganoMetallic Compounds, ICCOM-CNR, Via Madonna del Piano, 10 - 50019, Sesto F.no, Florence, Italy.*

[3] *Dept. of Chemistry "Ugo Schiff", Università di Firenze, via della Lastruccia 3-13, Sesto Fiorentino, Italy*

[4] *Dept. ChiBioFarm, University of Messina, 98166 Messina, Italy*

[5] *Consiglio Nazionale delle Ricerche-Istituto Officina dei Materiali (CNR-IOM), 34136 Trieste, Italy*

** gsantoriello@unisa.it*

Significance and Relevance

The electrochemical reduction of carbon dioxide (CO_2RR) is a transformative pathway to address greenhouse gas emissions while generating valuable chemical feedstocks. Fe-based Single-Atom Catalysts (SACs) offer a promising avenue due to their unique electronic and geometric properties. Recent advancements in computational and experimental techniques have enabled precise control over SAC structures, including the introduction of axial ligands[1]. This has been pivotal in enhancing their catalytic activity and selectivity[2–4]. By exploring tailored modifications, this work seeks to establish a framework for designing next-generation catalysts with improved performance, bridging fundamental insights and practical applications.

Preferred presentation: **Short Oral**

Introduction and Motivations

The pressing need for sustainable technologies has brought CO_2RR to the forefront of catalytic research. Traditional bulk catalysts often suffer from low selectivity and high overpotentials, limiting their industrial viability. SACs, particularly Fe-based variants, have emerged as game changers, enabling atomic-level precision in catalyst design. These systems exhibit unique properties due to their isolated active sites, which can be further tuned through axial ligand modifications. This study uses density functional theory (DFT) to investigate the impact of axial ligands on Fe-N-doped graphene SACs, focusing on the electronic and steric effects that influence CO_2 activation and product formation. The overarching goal is to identify design principles that enhance selectivity and reduce energy barriers, paving the way for the efficient conversion of CO_2 into valuable chemicals.

Results and Discussion

This study provides detailed insights into the impact of axial ligand modifications on the reactivity and selectivity of Fe-based single-atom catalysts (SACs) for CO_2 reduction reactions (CO_2RR). A key finding is that all examined axial ligands, including chloride, 2-aminopyridine, and 8-aminoquinoline, induce a "molecular lift," elevating the Fe center out of the graphene plane. This structural alteration significantly influences the electronic properties of the active site and, consequently, its catalytic behaviour modifying the oxidation and spin state configuration of the Fe center.

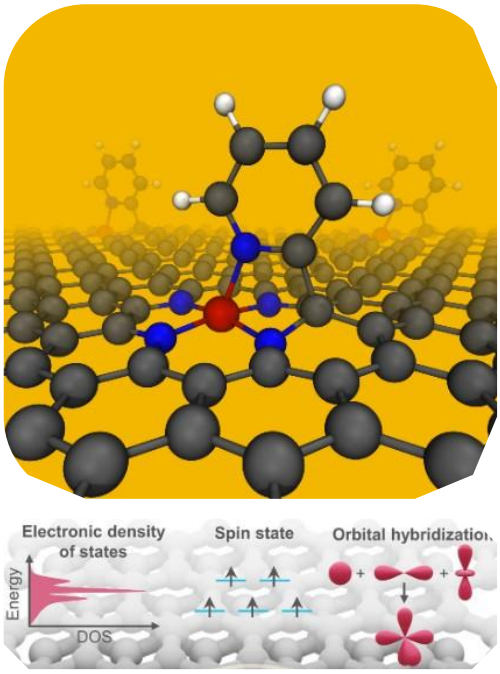
For instance, the electron-withdrawing nature of chloride ligand (Cl^-), lowering the binding affinity of *CO, a key intermediate in CO_2RR. This promotes efficient CO desorption, preventing active site poisoning and enhancing catalyst turnover rates. Nitrogen-containing ligands, such as 2-aminopyridine and 8-aminoquinoline, exhibit a dual effect: despite the increase of steric hindrance around the active site, they adjust the electronic properties of the Fe center by donating electron density that impact binding strength of intermediate species. Among these ligands, chloride achieves the highest selectivity over the parasitic hydrogen evolution reaction (HER), facilitating the desorption of *CO, a crucial aspect for catalyst selectivity. On the other hand, the steric effects of nitrogen-based ligands result in slightly higher potential determining step (PDS) energies, but they stabilize other intermediate states, potentially favoring subsequent reduction steps beyond CO production.

Adsorption energy calculations further emphasize the role of axial ligands in tuning reactivity. Chloride exhibits weaker binding with intermediates compared to nitrogen-based ligands, which aligns with its

observed superior performance in CO desorption. However, N-based ligands provide a better balance between the electronic stabilization of the Fe center and the steric flexibility needed to accommodate various intermediates during the catalytic cycle.

Overall, the introduction of axial ligands represents a versatile strategy to control the electronic and structural environment of Fe SACs, enabling precise tuning of catalytic properties. These findings highlight the potential for molecular lift engineering as a general approach to optimize SACs for CO_2RR, offering a pathway to achieve higher efficiency and selectivity in sustainable electrochemical processes.

Experimental validation corroborates these findings, showing that ligand-modified Fe-based SACs achieve superior performance in CO_2RR compared to unmodified systems. The synergy between computational predictions and experimental data underscores the feasibility of tailoring SACs for specific catalytic outcomes, providing a robust platform for the development of sustainable technologies.



References

(1) Lv, R.; Chen, S.; Wang, H. Axial Coordination Regulating Single Atoms for Enhanced CO2 Electroreduction. *ChemElectroChem* **2024**, *11* (13), e202300857. https://doi.org/10.1002/celc.202300857.

(2) Zhang, H.; Li, J.; Xi, S.; Du, Y.; Hai, X.; Wang, J.; Xu, H.; Wu, G.; Zhang, J.; Lu, J.; Wang, J. A Graphene-Supported Single-Atom FeN5 Catalytic Site for Efficient Electrochemical CO2 Reduction. *Angew. Chem.* **2019**, *131* (42), 15013–15018. https://doi.org/10.1002/ange.201906079.

(3) Li, Z.; Wu, R.; Xiao, S.; Yang, Y.; Lai, L.; Chen, J. S.; Chen, Y. Axial Chlorine Coordinated Iron-Nitrogen-Carbon Single-Atom Catalysts for Efficient Electrochemical CO2 Reduction. *Chem. Eng. J.* **2022**, *430*, 132882. https://doi.org/10.1016/j.cej.2021.132882.

(4) Ma, M.; Tang, Q. Axial Coordination Modification of M–N 4 Single-Atom Catalysts to Regulate the Electrocatalytic CO 2 Reduction Reaction. *J. Mater. Chem. C* **2022**, *10* (42), 15948–15956. https://doi.org/10.1039/D2TC02467E.

Acknowledgements
Lucia Caporaso acknowledges:
Italian Ministry of University and Research for funding the PRIN 2022 project: “Molecular Lift for the Control of the Metal Protrusion and Coordination Sphere in Single-Atom Catalysts for CO2 Electroreduction – MATISSE- with CUP: D53D23009150006

"Enhancing visible-light photocatalytic hydrogen evolution with sub-5 nm Fe-doped CeO_2 nanocrystals in confined spaces"

Giuseppina Iervolino[1], Olimpia Tammaro[2], Marco Fontana[2], Bruno Masenelli[3], Anne D. Lamirand[3], Vincenzo Vaiano[1], Serena Esposito[2]*

[1] *Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II 132, 84084 Fisciano, SA, Italy.*
[2] *Department of Applied Science and Technology and INSTM Unit of Torino – Politecnico, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy.*
[3] *INSA Lyon, Ecole Centrale de Lyon, CNRS, Universite Claude Bernard Lyon 1, CPE Lyon, INL, UMR5270, 69621 Villeurbanne, France*
* serena_esposito@polito.it

Significance and Relevance

This study demonstrates the effectiveness of the reverse micelle (RM) method for synthesizing sub-5 nm Fe-doped CeO_2 nanocrystals, enhancing visible-light photocatalytic hydrogen production from methanol solutions. The superior performance of RM-synthesized catalysts over conventionally prepared ones is confirmed through comprehensive characterization. Compared to literature reports on ceria-based catalysts, our Fe (2.5 mol%)-doped CeO_2 nanocrystals exhibit significantly higher normalized photocatalytic hydrogen evolution rates, despite the absence of noble metals and high-temperature calcination. Moreover, Fe-doped CeO_2 prepared by the RM method was stable for six reuse cycles.

Preferred and 2nd choice for the topic: H_2 storage and transportation, green H_2 production, hydrogen vectors, Photocatalysis and photoelectrocatalytic approaches, solar energy utilization
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster) Oral preferred or Short Oral

Introduction and Motivations

The efficiency and feasibility of photocatalytic water splitting hinge on the properties of the photocatalyst and the use of sacrificial agents[1]. With its unique electronic structure, high oxygen storage capacity, and excellent stability, ceria has emerged as a promising photocatalyst. However, there's a pressing need to tailor semiconductor-based materials to optimize the photocatalytic process and extend its activation to visible light[2].
In this scenario, the synthesis route is crucial in influencing nanocatalyst properties and defect engineering[3]. We developed a versatile and reliable one-pot reverse micelle process to address this challenge. This approach confines reactions within reverse micelles, allowing for precise control over the nucleation and growth of nanoparticles. Unlike traditional co-precipitation, this method enables the synthesis of monodisperse, nanometer-sized particles with tailored properties.

Materials and Methods

All syntheses were performed under mild conditions without the need for specialized equipment.
In a typical synthesis, Brij C10 surfactant was dissolved in cyclohexane at room temperature under stirring. A 0.5 M aqueous solution containing cerium and iron salts was slowly added dropwise to the oil phase to form water-in-oil (w/o) micelles.
An ammonia solution was then slowly added dropwise, and the mixture was stirred for 1.5 hours at room temperature. The resulting solid was filtered, washed, dried, and calcined at 120 °C for 6 hours. The amounts of cerium and iron were calculated to obtain a nominal composition expressed as a molar

% of iron equal to 0, 1, 1.5 and 2.5 and 5 mol%. CeO_2 and Fe (2.5 mol%)-CeO_2 catalysts were also prepared by conventional precipitation

Results and Discussion

X-ray diffraction initially revealed a clear distinction between samples prepared using reverse micelles and those obtained through conventional precipitation. The displacement of diffraction peaks to higher Bragg angles, as observed for RM catalysts, is indicative of a contraction of the crystal lattice. This provides compelling evidence for the successful isomorphic doping of CeO_2 with iron ions, wherein iron ions substitute for cerium ions within the lattice structure. In addition, XRD and TEM analyses confirmed the formation of ultra-small (~4 nm) photocatalyst nanocrystals within the confined space of reverse micelles. The RM system uniquely enhanced optical properties by facilitating the incorporation of large quantities of heteroatoms, thereby tuning the band gap with iron content, extending exciton lifetimes, and modulating Ce^{3+} and Vo defect concentrations, as evidenced by Raman, UV-Vis, and photoluminescence spectroscopies. Moreover, RM synthesis yielded significantly higher surface areas compared to conventional methods.

Photocatalytic hydrogen production reached a maximum of 7566 µmol L^{-1} for RM samples with 2.5 mol% iron doping in the CeO_2 lattice, indicating this as the optimal doping level for this synthesis method, Figure 1. Fe (2.5 mol %) CeO_2 photocatalyst exhibited excellent stability, maintaining consistent photocatalytic hydrogen production over six reuse cycles. A proposed visible-light-driven photocatalytic mechanism for hydrogen evolution from methanol aqueous solution was supported by D_2O experiments and band alignment considerations. The mechanism involves the reduction of H^+ by conduction band electrons and the oxidation of methanol by valence band holes

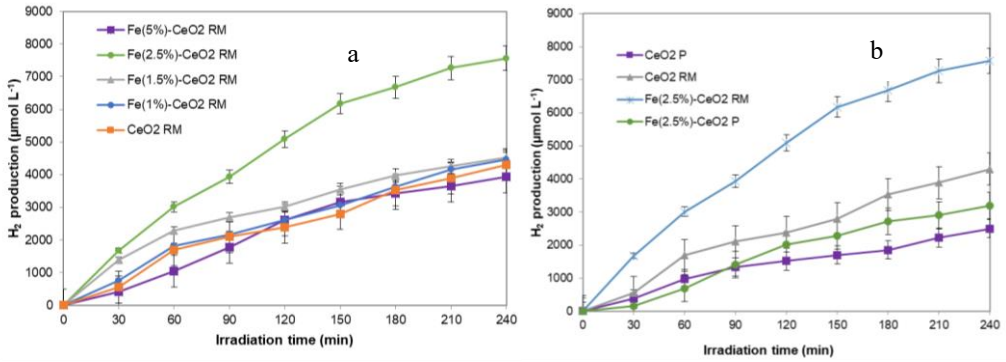


Figure 1 Hydrogen evolution under visible light for a) CeO_2 and Fe-CeO_2 photocatalysts prepared by reverse micelle (RM) and b) CeO_2 and Fe-CeO2 photocatalysts prepared by conventional precipitation (P).

References

1. K. Maeda, *J. Photochem. Photobiol*., **2011**, C 12 (2011) 237–268.
2. O. Tammaro, R. Paparo, M. Chianese, I. Ritacco, L. Caporaso, M.F. Camellone, B. Masenelli, A.D. Lamirand, J.-M. Bluet, M. Fontana, G. Pinto, A. Illiano, A. Amoresano, M. Di Serio, V. Russo, S. Esposito, *Chem. Eng. J.* **2024** 479, 147909.
3. C Sun, H L. Liquan Chenab, *Energy Environ. Sci*., **2012**, 5, 8475.

Photocatalytically-regenerable hyper-crosslinked microporous adsorbent

Pierluigi Lasala,[1] Khalid Tahla,[1] Antonio Maglione,[2] Antonia Cerbone,[2,3] Serena Catullo, [1] Gaia Raffaele, [1] Ombretta Giancaspro,[1] Antonella Milella,[1] Ilaria De Pasquale,[4] Rachele Castaldo,[2] Gennaro Gentile,[2] Maria Lucia Curri, [1,.4,5] Elisabetta Fanizza[*,1,.4,5]

[1]*University of Bari A. Moro, Department of Chemistry, Via Orabona 4, 70126 Bari, Italy*
[2] *CNR- Institute of Polymers, Composites and Biomaterials (IPCB), Via Campi Flegrei 34, 80078 Pozzuoli (NA), Italy*
[3] *University of Naples, Department of Chemical Science, Strada Comunale Cinthia, 26, 80126, Naples, Italy*
[4] *CNR-Institute for chemical and physical processes (IPCF), Via Orabona 4, 70126 Bari, Italy*
[5] *National Interuniversity Consortium of Materials Science and Technology, INSTM, Bari Research Unit, 70126, Bari, Italy*

** elisabetta.fanizza@uniba.it*

Significance and Relevance

This work aims to face the critical concern regarding water contamination by developing new adsorbents with high adsorption efficiency and easy solar-light activated photocatalytic regeneration for repeated use, through environmental friendly and cost-effective processes, targeting sustainable contaminants removal from wastewater. Adjoining to the adsorption function the solar light induced photocatalytic activity, afforded by decorating the hyper-crosslinked microporous adsorbent with purposely engineered metal oxide NPs, will provide a sustainable solar light-driven in situ regeneration.

Preferred and 2nd choice for the topic: Photocatalysis and photoelectrocatalytic approaches, solar energy utilization (Preferred); Water treatment (2nd choice)
Preferred presentation: (Oral only)

Introduction and Motivations

Adsorption, recently greatly stimulated by availability of high specific surface area materials, has grabbed the attention of scientists as a versatile, cost-effective option for relatively effortless large-scale water treatment. However, adsorbent disposing may have an adverse environmental impact that should be mitigated through regeneration and reuse processes, usually employing high-cost procedures. The validation of an adsorbent cannot be limited to prove the efficiency of the adsorption process but it must also address its lifetimes, related to the level of its reusability, the cost of regeneration treatments required to reactivate its adsorption capacity, and their environmental effects. This works aims at addressing this issue by proposing a new concept of smart adsorbents where enhanced adsorption is combined to in situ regeneration by solar-activated heterogeneous photocatalysis for an energy-efficient removal of contaminants. Metal oxide nanoparticles, synthesized by colloidal approaches, and purposely engineered to show absorption in the visible range of the electromagnetic spectrum, have been tested as photocatalysts and purposely combined to a biobased hyper-crosslinked microporous adsorbent.

Results and Discussion

Solution-phase approaches under mild reaction conditions have been exploited towards the design and fabrication of metal oxide nanoparticles (TiO_2, CeO_2) with and without dopants, engineering size and surface defects for tuneable physical and chemical properties towards excellent solar-light activated photocatalytic properties. Colloidal chemistry simple methodologies have been developed, including in-situ synthesis of the colloidal nanoparticles in the presence of microporous adsorbent or ex-situ approach, where pre-synthesized nanoparticles have been let to adsorb on the adsorbent, to adjoin the photocatalytic properties to a purposely synthesized hyper-crosslinked microporous adsorbent (Figure 1). The nanoparticle-modified adsorbent has been evaluated paying particular

attention to the adsorbent structural stability, adsorption properties, nanoparticle loading and photocatalytic performance, since all these factors may effectively impact the adsorption and regeneration technology. Different aspects involved in the combination of large specific surface area adsorbents with nanometer-sized photocatalyst have been studied. The regeneration process of the adsorbent obtained photocatalytically under sunlight can be kinetically promoted by adsorption, the broad absorption of the adsorbent can extend the light response of the photocatalyst to the visible region improves the utilization of solar energy, the aggregation of the nanoparticles can be limited thanks to their anchoring on the adsorbent. In-depth investigation by structural, morphological, chemical and optical characterization have been exploited to assess the best photocatalyst candidate, understand the photocatalytic mechanisms involved in the contaminant degradation and, hence adsorbent regeneration, and the suitable functionalization procedure selected.

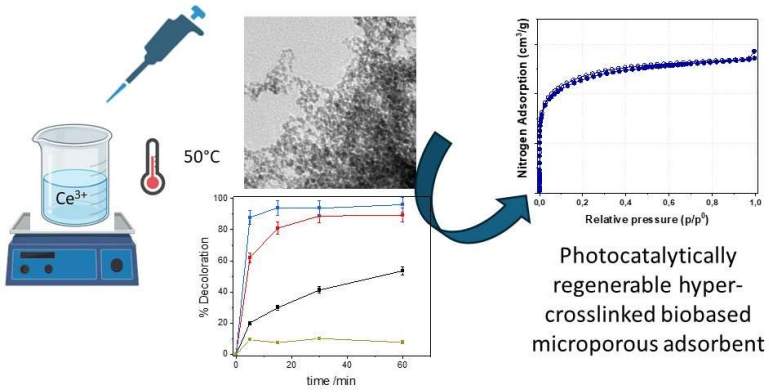


Figure 1. Schematic representation of the work objective: development of colloidal nanosized photocatalyst with suitable morphologies and photocatalytic properties, adjoined to a high specific surface area microporous adsorbent towards the fabrication of a highly efficient adsorbent regenerable by solar-light activated photocatalysis

Acknowledgements

This work has been supported by the European Union through Next Generation EU, Mission 4 Component 1, from MUR within PRIN call 2022 PNRR, Project title: Photocatalytically regenerable hierarchically porous adsorbents for efficient water treatment PHOTOPAD, P2022FP2W4, 2023-2025CUP B53D23027540001)

ADDITIVE-FREE PHOTOCHEMICAL UPCYCLING OF BIO-BASED (MICRO)PLASTICS INTO VALUE ADDED CHEMICALS

Athanasia KOTSARIDOU[1*], Dimitrios A. GIANNAKOUDAKIS[1], Konstantinos TRIANTAFYLLIDIS[1]
[1]*Aristotle University of Thessaloniki, Department of Chemistry, Thessaloniki, Greece*
** e-mail corresponding: nancykotsa7@gmail.com*

Significance and Relevance

Our approach targets to the development of sustainable methods for biobased (micro)plastics upcycling with the smallest environmental footprint, through additive-free heterogeneous photocatalysis, enabling the conversion of plastic waste into value-added chemicals. This work demonstrates as proof of concept for low-cost, energy-efficient, easy to operate, and environmentally friendly strategy to the controlled breakdown of specific bonds in polymers, as for instance C-C bonds in the cased of bio-based polylactic acid (PLA). The predominately desired compounds are lactic acid and pyruvic acid, although some additional compounds are also welcome. The key parts of the processes are on the one hand to optimize crucial experimental parameters (like solvent, temperature, duration, nature of the light irradiation etc.) and on the other to design and develop advanced nano-photocatalysts of specific physicochemical features. Regarding the novel photocatalytic nanostructured materials, they should be designed to have a high specific surface area, large pores volume, and an abundance of surface functional groups, especially acid ones, since they are expecting to ultimately improve the overall photocatalytic efficiency.

Preferred and 2nd choice for the topic: Photocatalysis and photoelectrocatalytic approaches, solar energy utilization and Green chemistry and biomass transformation, renewable resources conversion
Preferred presentation: Poster

Introduction and Motivations

Plastic waste ending up in landfills or released into the natural environment due to insufficient recycling and reuse technologies poses serious threats to ecosystems and human health. Bio-based, biodegradable plastics like PLA have been proposed as a solution, and their demand is expected to soar, with global annual production projected to triple in 2 years. Although PLA is assumed as a promising alternative to traditional petroleum-based plastics, its degradation remains significantly slower than desired[1]. Meanwhile, PLA nature bio-decomposition releases predominately CO_2 and H_2O, resulting in carbon emissions. Hence, it is an urgent need for novel and efficient catalytic recycling method that can convert PLA into value-added chemicals. Photocatalysis offers a green and sustainable approach addressing this challenge, providing an advantage over conventional plastic recycling, which often involves high energy input, toxic solvents and strong acidic or basic conditions[1]. To trigger the potential of a targeted photocatalytic PLA upcycling, we synthesized novel nanomaterials based on our previously experience[2,3].

Materials and Methods

Herein, we test a wide range of commercial and novel home-made nano-photocatalysts including TiO_2 P25 and P90 nanoparticles, synthesized titanate nanotubes, metal-doped titanium oxide nanoparticles and nanotubes (Mn, Pt, Cu), zinc oxide nanoparticles, bulky and nanosized defected graphitic carbon nitride (g-C_3N_4), carbon quantum dots etc. The materials were synthesized using different protocols including hydrothermal, ultra-slow precipitation, and calcination methods, while they were previously characterized via various techniques (XRD, SEM, N_2-sorption, DR UV-Vis, TA) to determine their physicochemical properties. Photocatalytic tests of PLA upcycling were performed in different solvents with emphasis on using the “greenest” ones, namely water, acetonitrile or mixtures of them. Various other parameters were explored with the most vital to be the catalyst/plastic ratio (1/10), nature of irradiate light of specific wavelengths (UV-A (375 nm), violet (427 nm), royal blue (425 nm), green (525 nm) and their combinations.

Results and Discussion

Among the various tested materials, some synthesized materials showed capable to initiate the photocatalytic PLA conversion. In the case of water as solvent and only by the heat provided by the

LEDs (max 50 °C), PLA microplastics (size range: 500-1000 μm) was found being very photo-stable, while the commercial benchmark TiO_2 P25 showed a very limited PLA conversion under UV-A light without the addition of any additive. Our developed titania oxide/hydroxide nanoparticles prepared by ultrasound-assisted ultra-slow precipitation (Ti-US) demonstrated a 72% higher PLA conversion comparing to P25. Additionally, the novel Ti-US, aside from producing valuable lactic and formic acid, contributed also to the production of acetic acid, thus increasing the range of chemicals generated through the photocatalytic upcycling of PLA. This nano-architectured material has a surface area above 400 m^2/g and the pores volume exceed 0.5 cm^3/g. In addition, it possesses a significant volume of micropores (~0.08 cm^3/g). Ultimately important are also the nanoparticles' (NPs) morphological, structural, and surface chemical features. The rough external "sponge-like" surface of the NPs has a high density of SFGs, predominately acidic, with the surface pH to be found equal to 3.0. The acid surface environment is anticipated to play a key role on interacting with the PLA particles and acting as a "bridge" for the transfer of the photo-induced charges (e^-/h^+), initiating polymer's C-C cleavage without the need any acidic additive.

Even though the presented conversions are not assumed very high, these results indicate that further optimization of the process (maybe even addition of some environmental-friendly additives like molecular oxygen) and above all materials/composites further development could improve the yield of the sustainable photocatalytic plastic up-cycling. This fact can be supported by the best results obtained from a multi-doped titanate nanotubes composite (TiNTNbs-gC_3N_4CuPt). Pure titanate nanotubes or graphitic carbon nitride barely reached a 10% PLA conversion separately, while addition of Pt or Cu to the nanotubes did not impact positively the PLA conversion. On the contrary, the TiNTbs nanocomposite with g-C_3N_4, co-doped with Pt and Cu (TiNTbs/gC3N4CuPt) showed a very promising PLA conversion of almost 20 %.

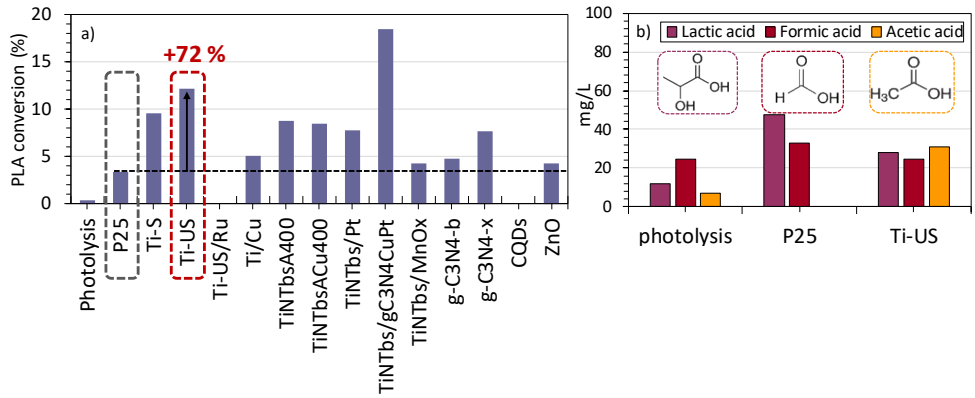


Figure 1. Photocatalytic upcycling of PLA with synthesized nanomaterials a) PLA conversion, b) products of PLA photodegradation (Experiment conditions: 15 mL solution of PLA/H_20 1% w/v, 1 g/L catalyst, 375 nm, 50 °C, 400 rpm, 96 h).

References

1. T. Uekert,Kasap H., E. Reisner. Photoreforming of Nonrecyclable Plastic Waste over a Carbon Nitride/Nickel Phosphide Catalyst. Journal of the American Chemical Society 2019, 141 (38), 15201–15210.
2. D. A. Giannakoudakis, K.Vikrant, A. P.LaGrow, D. Lisovytskiy, K. H.Kim, T. J.Bandosz, & J. Carlos Colmenares. (2021). Scrolled titanate nanosheet composites with reduced graphite oxide for photocatalytic and adsorptive removal of toxic vapors. Chemical Engineering Journal, 415(December 2020), 128907. https://doi.org/10.1016/j.cej.2021.128907
3. D. A. Giannakoudakis et. al., 2021. Boosting the Photoactivity of Grafted Titania: Ultrasound-Driven Synthesis of a Multi-Phase Heterogeneous Nano-Architected Photocatalyst. Advanced Functional Materials, 31(1).

Acknowledgements

"This project is carried out within the framework of the National Recovery and Resilience Plan Greece 2.0, funded by the European Union – NextGenerationEU (Implementation body: HFRI, Project No.: 015949)."

AN IRON-BASED BIOCHAR-SUPPORTED CATALYST FOR DICLOFENAC DEGRADATION

Marianna Gualiano[1], Christian de los Ríos[2], Karla Jiménez-Bautista[2], Virginia Muelas-Ramos[2], Ana Bahamonde[3], Cinzia Cristiani[1], Simone Pedrazzi[4], Marco Puglia[4], Daphne Hermosilla[2], Antonio Gascó[2]

[1]Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta"- CMIC, Politecnico di Milano, Piazza Leonardo Da Vinci 32, 20133, Milano, Italy
[2]G-Aqua Research Group, Universidad Politécnica de Madrid, Escuela Técnica Superior de Ingeniería de Montes, Forestal y del Medio Natural, Calle José Antonio Novais 10, 28040 Madrid, Spain
[3]Instituto de Catálisis y Petroleoquímica, Consejo Superior de Investigaciones Científicas, Calle de Marie Curie 2, 28049 Madrid, Spain
[4]Department of Engineering "Enzo Ferrari", Università degli Studi di Modena e Reggio Emilia | UNIMO, Via Università 4, 41121 Modena

Significance and Relevance

Photocatalytic degradation is considered an efficient strategy for the removal of organic pollutants. In this study, biochar— the carbonaceous by-product of thermochemical processes such as pyrolysis and gasification—is proposed as an innovative and sustainable support for catalyst development. Biochar advantageous characteristics, including high surface area and porous structure, make it an ideal candidate for developing a Fe-biochar catalyst aimed at removing Diclofenac (DFC) from contaminated water sources.

Preferred and 2nd choice for the topic: Water treatment, Photocatalysis and photoelectron catalytic approaches, solar energy utilization
Preferred presentation: Oral

Introduction and Motivations

Diclofenac (DFC) is a non-steroidal anti-inflammatory drug commonly found in wastewater and surface water, leading to negative effects on the environment and ecosystems[1]. Various strategies exist for removing DFC from wastewater; among these, photocatalytic degradation is considered one of the most promising technologies. For the photocatalyst several materials have been proposed as supports for the iron active phase[2]. However, due to concerns about cost and environmental impact, there is a growing need for greener and circular alternatives. In this context, biochar— a carbon-rich by-product of biomass gasification/pyrolysis—emerges as a potential eco-friendly substitute of conventional supports thanks to its high porosity and high surface area.

Materials and Methods

An iron-based biochar-supported catalyst (Fe-T) was prepared using a commercial biochar (T) obtained from fir tree biomass (supplied by Cogen, Terni (IT)). The catalyst was prepared according to the incipient wetness technique[3] using $Fe(NO_3)_3 \cdot 9H_2O$ as Fe precursor, to reach a final Fe nominal content of the 2% (w/w) on the total weight of the sample. Pristine biochar and Fe-T catalyst were characterized by means of Zeta Potential (ZP), Surface Area (SA), Pores Volume (PV), XRPD, SEM-EDX, FT-IR, TG-DTG. Photocatalytic and adsorption tests were performed in batch, at RT, and atmospheric pressure. In a typical photocatalytic experiment, 0.1 g of the Fe-T catalyst were suspended in 100 mL of deionized water. Subsequently, 100 $mg \cdot L^{-1}$ of DFC were added to the suspension just before it was illuminated with 367 nm UV light, and the stoichiometric H_2O_2 content for full DFC oxidation was added. In case of DFC adsorption by pristine biochar (T) and Fe-T, the reaction occurred without UV light and H_2O_2 application. Reaction progress was followed by collecting aliquots of the suspension with a syringe equipped with a PTFE filter at different time intervals. The residual amount of DFC in the solution was analyzed by HPLC equipped with a C18 column.

Results and Discussion

Pristine biochar is characterized by a high surface area (658 m^2/g) where micropores contribution is dominant, and such morphological characteristics are preserved upon iron impregnation (Table 1).

Table 1. Morphological properties of biochar (T) and the iron-based biochar-supported catalyst (Fe-T).

Material	SA_{BET} m^2/g	SA_{micro} m^2/g	SA_{ext} m^2/g	Vp_{micro} cm^3/g	Vp_{meso} cm^3/g	Vp_{Macro} cm^3/g
T	658	590	68	0.26	0.11	0.22
Fe-T	613	556	55	0.25	0.08	0.38

SEM-EDX analysis shows that T and Fe-T before the photocatalytic reaction have similar morphological structure, characterized by channels and pores of different dimensions, typical of biochar (Figure 1 a-c). Moreover, Fe is homogeneously distributed in Fe-T (fig. 1d).

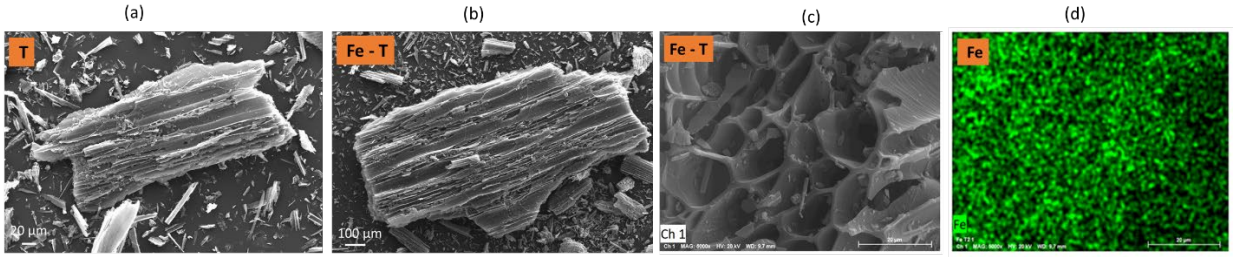


Figure 1. SEM analysis of: (a) the support (T) at 500X, and of the catalyst (Fe-T) at different magnifications (b) 250X, (c) 5,000 X; (d) EDX map of Fe ions in Fe-T catalysts.

Both the pristine support and the catalyst are able to adsorb up to 60 % of DFC from a solution containing 100 $mg \cdot L^{-1}$ in 1 h (Figure 2a). Thereafter, a plateau is reached, and no further adsorption occurred. When the photocatalytic reaction is performed, further DFC removal was observed up to 99% of DFC (Figure 2b). However, a low H_2O_2 consumption (<25%; Figure 2c) suggests that adsorption might always be co-present and predominant. In any case, the photocatalytic reaction addressed the total removal of DFC, which was not possible by adsorption standalone.

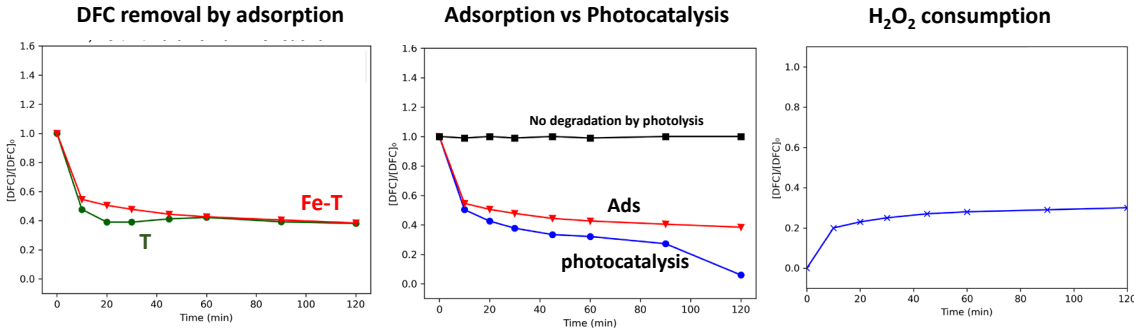


Figure 2. Removal of DFC by T and Fe-T via a) adsorption, b) photocatalysis, and c) H_2O_2 consumption in this process.

References

1. J.M. Angosto *et al*. Water 2020, 12, 3567. https://doi.org/10.3390/w12123567
2. G. Ren *et al*. Nanomaterials 2021, 12;11(7):1804. https://doi: 10.3390/nano11071804
3. M. Campanati *et al*. Catalysis Today,2003, 77, 4. https://doi.org/10.1016/S0920-5861(02)00375-9

Acknowledgements

Project PID2020-114918RB-I00 (PHOTOPREBIO), funded by MCIN/AEI/ 10.13039/501100011033; and PID2021-124021OB-I00 (URBRAINTREAT), funded by MCIN/AEI/10.13039/501100011033 & "ERDF: A way of making Europe"

Photocatalytic nanocomposites based on pyrene functionalized reduced graphene oxide in situ decorated with TiO_2 nanorods

C. Ingrosso,[1] A. Disha,[2] M. Dell'Edera,[1] I. De Pasquale,[1] G. V. Bianco,[3] A. Milella,[2] A. Grandolfo[1,4,5] E. Mesto,[5] E. Schingaro,[5] M. Striccoli,[1] E. Fanizza,[1,2] R. Comparelli,[1] M. L. Curri[1,2]

[1]*CNR-IPCF Sez. Bari, c/o Dept. of Chemistry, Università degli Studi di Bari, via Orabona 4, 70126 Bari, Italy*

[2]*Dept. of Chemistry, Università degli Studi di Bari, via Orabona 4, 70126 Bari, Italy*

[3]*CNR-NANOTEC, c/o Università degli Studi di Bari, Via Orabona 4, 70126 Bari, Italy*

[4]*Dept. of Electrical and Information Engineering, Polytechnic of Bari, Via Amendola 126/b, 70126 Bari, Italy*

[5]*Dept. of Earth and Geoenvironmental Sciences, Università degli Studi di Bari, via Orabona 4, 70126 Bari, Italy*

**c.ingrosso@cnr.it*

Significance and Relevance

Novel hybrid nanocomposites formed of 1-pyrene carboxylic acid (PCA) functionalized High Porous Reduced Graphene Oxide (PCA-HPRGO) sheets, decorated with oleic acid (OLEA)-coated TiO_2 nanocrystals (NCs) of different morphologies, spherical (Ndots) and nanorods (NRs), were synthesized by an *in situ* colloidal route, and were tested in the photodegradation of methyl red (MR) under UV-light irradiation, and of nalidixic acid (NA) under solar-light irradiation. Their photocatalytic activity has been evaluated against neat TiO_2 NCs and commercial TiO_2 P25 and discussed in terms of electronic level alignment between the hybrid nanostructure components, considering the role of the PCA anchoring molecule at the interphase.

Preferred and 2nd choice for the topic: Water treatment

Preferred presentation: Oral preferred or Short Oral

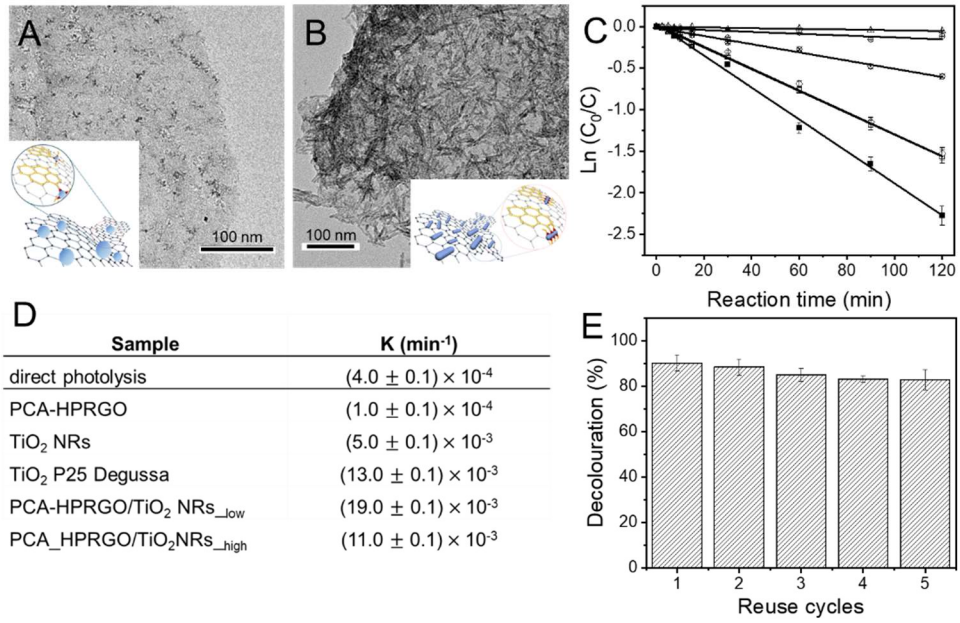
Introduction and Motivations

The combination of TiO_2 nanocrystals (NCs) with graphene derivatives is a very promising strategy to develop photocatalytic nanostructures for environmental remediation [1]. NC TiO_2, in anatase phase, is among the most widely investigated photocatalysts. Due to its wide band gap, however, only 4% of solar light can generate electron–hole pairs in TiO_2, that, migrating to its surface, act as redox source ultimately leading to photocatalytically active species. In addition, the short mean path of its electrons increases electron-hole recombination rate, thus decreasing its photocatalytic efficiency. The development of nanocomposites based on graphene derivatives and TiO_2 nanoparticles is a cost-effective innovative solution to solve these issues. Graphene derivatives behave as sensitizers of the semiconductor under Vis-light irradiation, transferring electrons from their Fermi level to the conduction band of TiO_2 and allowing fast exchange of photo-induced charges. Under UV-light, instead, photo-generated electrons in the conduction band of TiO_2 are spontaneously transferred to graphene, whose high charge mobility may efficiently suppress exciton recombination at the nano-oxide defects. Besides, to limit electron-hole pairs recombination in photoexcited TiO_2, the use of anisotropic nanostructures with an elongated morphology may be useful [2].

Results and Discussion

TiO_2 Ndots and NRs were demonstrated to heteronucleate and growth onto the –COOH groups of the PCA-HPRGO sheets (Figure 1A-B), in presence of oleic acid (OLEA) surfactant, without deteriorating HPRGO's structure, as demonstrated by Raman spectroscopy [1]. Morphology and UV-Vis absorption spectroscopy properties of the resulting nanocomposites were found affected by the TTIP:OLEA molar ratio and the PCA-HPRGO:TTIP w/w, and the supply mode of the TMAO base [1], which catalyzes the condensation reaction of the nano-oxide defining its morphology [1]. PCA, which firmly anchors onto the HPRGO platform by aromatic π-π stacking interactions, was found to act as a coordinating site contributing with OLEA in controlling formation of the NCs in anatase crystalline phase [1], and as a mediator of their electron coupling with HPRGO, which was assessed by XPS investigation [1]. The TiO_2 Ndots based nanocomposites showed a much lower coating density than the NRs based ones and a poorer quality, due to the different synthesis conditions (Figure 1A). Therefore, considering also the

higher photocatalytic activity expected for the TiO_2 NRs based nanocomposite due to the NCs anisotropy [2], the photocatalytic activities of this type of nanocomposites, which were prepared at 1:100 and 1:50 PCA-HPRGO:TTIP w/w (PCA-HPRGO/TiO_2 $NRs_{_low}$, PCA-HPRGO/TiO_2 $NRs_{_high}$), were investigated against those of PCA-HPRGO, OLEA-coated TiO_2 NRs and commercial TiO_2 P25 Degussa control samples (Figure 1D). The efficiencies of the photocatalysts were evaluated from the respective reactions of the photocatalytic degradation of MR (Figure 1C), estimating the apparent kinetic constants (Figure 1D) [1].



Sample	K (min^{-1})
direct photolysis	$(4.0 \pm 0.1) \times 10^{-4}$
PCA-HPRGO	$(1.0 \pm 0.1) \times 10^{-4}$
TiO_2 NRs	$(5.0 \pm 0.1) \times 10^{-3}$
TiO_2 P25 Degussa	$(13.0 \pm 0.1) \times 10^{-3}$
PCA-HPRGO/TiO_2 $NRs_{_low}$	$(19.0 \pm 0.1) \times 10^{-3}$
PCA_HPRGO/$TiO_2$$NRs_{_high}$	$(11.0 \pm 0.1) \times 10^{-3}$

Figure 1. TEM micrographs of A) PCA-HPRGO/TiO_2 ndots and B) PCA-HPRGO/TiO_2 NRs. C) XRD, D) kinetic constants (K) of the investigated photocatalysts, E) reusability tests for the decolouration of MR assisted by PCA-HPRGO/TiO_2 $NRs_{_low}$.

Figure 1D shows that the photocatalytic activity of PCA-HPRGO/TiO_2 NRs i. depends on the relative mass fraction of HPRGO in the nanocomposite, decreasing with the increase of the PCA-HPRGO:TTIP w/w, ii. is higher than that of PCA-HPRGO, neat TiO_2 NRs and commercial TiO_2 P25, and iii. is almost preserved maintaining at more than 80% after five successive photocatalytic cycles (Figure 1E). Under solar-light irradiation, the overall photoactivity of the nanocomposite deteriorated [1]. Such an effect can be ascribed to the p-doping effect of the PCA linker that is expected to increase the Schottky barrier to the transfer of photoinduced electrons from PCA-HPRGO to the TiO_2 NRs [1]. Such an unexpected outcome, opposing the anticipated enhancement from the combination with RGO, can reasonably be attributed to the adverse effect of PCA. This work, while confirming the potential of the developed PCA-HPRGO/TiO_2 NRs hybrid nanocomposite in the degradation of organic pollutants under UV-light for water purification and air remediation applications, as well as in other relevant photocatalytic applications, contributes also to clarifying a more fundamental query on the role of the organic linkers in affecting electron charge transfer processes between the hybrid nanostructure components.

References

1. C. Ingrosso et al. *J. Photochem. & Photobiol., A: Chem.* **2025**, 460, 116149
2. L. Manna et al. *J. Am. Chem. Soc*. **2002**, 124, 7136

Acknowledgements

This research was funded by the European Union – NextGeneration EU from the Italian Ministry of Environment and Energy Security POR H2 AdP MMES/ENEA with involvement of CNR and RSE, PNRR - Mission 2, Component 2, Investment 3.5 “Ricerca e sviluppo sull’idrogeno”, CUP: B93C22000630006.

Innovative Photoelectrocatalytic filter for Recirculating Aquaculture Systems

Luca Maistrello,[1] Simone Livolsi[1] Eleonora Buoio,[2] Daniela Bertotto[3], Giuseppe Radaelli[3], Alessia di Giancamillo,[2] Annamaria Costa,[2] Gian Luca Chiarello*,[1]

[1] *Department. Of Chemistry, University of Studies of Milan, Via Golgi 19 20133, Milan*

[2] *Department of Veterinary Medicine and Animal Sciences, University of Milan, 26900 Lodi, Italy*

[3] *Department of Comparative Biomedicine and Food Sciences University of Padova, Italy.*

** gianluca.chiarello@unimi.it*

Significance and Relevance

This work aims to study an innovative photoelectroncatalytic (PEC) water treatment in recirculating aquaculture system (RAS) for fish farming alternative to the conventional biological filters used so far. This novel filter exploits the UV-electrochlorine advance oxidation process and has been tested *in vivo* in order to study the effectiveness and the biocompatibility of this technology in presence of living fishes (rainbow trout). This PEC reactor also has the advantage of being easily implemented within the existing UV sterilizer, thus reducing overall operating costs.

Preferred and 2nd choice for the topic: Water treatment, Photocatalysis and Photoelectrocatalytic approaches, solar energy utilization.
Preferred presentation: Oral only

Introduction and Motivations

Ammonia poses a threat to biodiversity in aquatic environments, having toxic effects on fish and animals living in freshwater and seawater[1]. Land-based aquaculture uses recirculating aquaculture systems, which take advantage of biological filters to oxidise ammonia to nitrite ion NO_2^- and the much less toxic nitrate ion NO_3^-. Periodical replacement of water leads to the emission in the environment of large amounts of nitrogen rich wastewater, contributing to eutrophication in fresh and seawater. It's possible to couple a semiconductor to the already present Hg-UV lamp setups in fish farming plants, to construct a photoelectrochemical reactor which exploits the UV-electrochlorine advanced oxidation process. The semiconductor coated anode illuminated by the lamp oxidizes chloride ions naturally present in fresh- (or sea-) water, the generated highly reactive chlorine species oxidize the ammonia released by fish and convert it into NO_3^- and the more inert N_2.[2]

Materials and Methods

Synthesis of the photoanode material is achieved through an easily scalable anodization procedure yielding highly active thin film of TiO_2 arranged in self-assembled vertical nanotubes arrays from metal Ti metal substrate.[3] Ti mesh tubes of 4 cm diameter and 39 cm long are anodized in an electrolyte solution of 0.2 M HF, 8 M H_2O in ethylene glycol at 30 V for 1.5-6 h. Finally, the meshes are rinsed and sonicated in absolute ethanol, following calcination at 450°C for 2 h with heating ramp of 10 °C min^{-1}. Preliminary tests were performed in a 1.08 L glass lab scale reactor (fig. 1). A metal Ti mesh tube surrounding the TiO_2 coated photoanode is used as counterelectrode, water is recirculated by a rotary pump from a 2.5 L tank. Ammonia degradation tests are run on 5 mmol L^{-1} KCl and 100 ppm NH_3 solutions at 4 V potential bias. Periodical analysis of NH_4^+, NO_2^- and NO_3^- by ion chromatography allows to trace ammonia conversion and selectivity towards the NO_2^- and NO_3^- N_2 products. *In vivo* tests have been performed with six individual tanks (three control and three treated groups), with a recirculating flow rate set at ca. 120 L/h. A total of 375 g of juvenile rainbow trout (around 60 individuals/tank, 16

°C, 10 L/14 D photoperiod), at 7.5 kg/m3 density and fed twice daily (0.7% body weight) was distributed in each tank at the beginning of the test.

Results and Discussion

Anodization of the Ti metal meshes in presence of HF yields a TiO_2 thin film layer arranged in a vertical nanotube array as shown in the SEM image in fig. 1. The film composition is anatase, and show very high photoactivity in the UV range at $\lambda < 380$ nm. Ammonia concentration linearly decreases overtime while NO_2^- accumulates over the first 2 hours and is then further consumed, NO_3^- concentration increases during the whole experiment as ammonia is converted. The concentration profiles are typical of consecutive reactions where NO_2^- is the first intermediate and is then consumed to make the NO_2^- end product. Selectivity toward nitrate only reaches up to 50% of the total ammonia converted, and the remaining nitrogen is converted to N_2. Optimization of the synthesis procedure by changing the anodization time from 1.5 h to 6 h allows to increase the photocurrent and increase the overall PEC performance of the reactor.

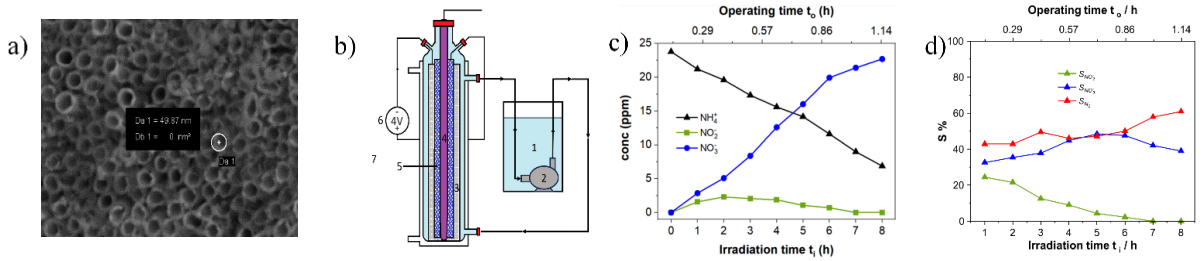


Figure 1 SEM image of the anodized Ti mesh (a), lab-scale PEC setup (b), variation of NH_3 (black), NO_2^- (green), and NO_3^- (blue) concentration (c) and selectivity to NO_2^- (green), NO_3^- (blue), N_2 (red) (d) during the PEC experiment in KCl 5 mM.

By contrast, only a slight X_{NH3} (ca. 10 %) is observed in K_2SO_4 electrolyte solution. These results suggest that chlorine has a crucial role in the ammonia PEC oxidation process: photo-generated holes on the photoanode surface can oxidize Cl^- to $Cl^\bullet$ (electro-induced process), which is a reactive radical able to oxidize ammonia through the formation of different chloramines intermediates.

The in-vivo tests confirmed the photocatalytic performances obtained in lab scale and the histological analysis made on the fishes did not revealed any pathological alteration in the gills and liver of both groups. The superoxide dismutase (sod1), glutathione reductase (GR), glutathione peroxidase (GPx1), and Tumor necrosis factor (TNFa) gene expressions were significantly higher in the control group than in the PEC-treated group, while the Heat shock protein 70 (Hsp70) expression did not show any difference in the two groups. These results indicate that the use of PEC filters has a positive effect on water quality, compared to the use of conventional biological filters, inducing a high level of welfare in rainbow trout.

References

1. R. Crab, et Al., Aquaculture **2007**, 270, 1–14
2. S. Livolsi et al. Catal. Today **2023**, 113996, 413-415
3. G. L. Chiarello et al., ACS Catal **2016**, 6, 1345–1353
4. E. Buoio, el al. Sustainability, **2022**, 14, 9067
5.

Acknowledgements

This work received financial support from the PRIMA 2019 FishPhotoCat Project. The Istituto sperimentale Lazzaro Spallazani in Rivolta D'adda is acknowledged for the support during the *in vivo* tests.

Sustainable ammonia synthesis using graphene/$MnFe_2O_4$-based gas-diffusion electrodes via photo-, electro-, and photo-electro-catalytic routes

Clécia ANDRADE DOS SANTOS[1,2], Matteo MICELI[*,3], Luciane PIMENTA CRUZ ROMÃO[2], Maria Valnice BOLDRIN ZANONI[2], Siglinda PERATHONER[3], Gabrieli CENTI[3], Claudio AMPELLI[3]

[1] *São Paulo State University (UNESP), Institute of Chemistry, Araraquara, Brazil.*
[2] *National Institute of Alternative Technologies for Detection, Toxicological Evaluation and Removal of Micropollutants and Radioactive Substances (INCT-DATREM), São Paulo State University (UNESP), Institute of Chemistry, Araraquara, Brazil.*
[3] *University of Messina (UNIME), CASPE/INSTM and ERIC aisbl, Department of Chemical, Biological, Pharmaceutical and Environmental Sciences (ChiBioFarAm), Messina, Italy.*
** matteo.miceli@unime.it*

Significance and Relevance

In this work, dinitrogen (N_2) molecule was converted to ammonia (NH_3) by electro-catalytic (EC), photo-catalytic (PC) and photo-electro-catalytic (PEC) approaches, using novel gas-diffusion electrodes (GDEs) based on $MnFe_2O_4$ or graphene (GH)-$MnFe_2O_4$ semiconductors supported on gas diffusion layers (GDLs). Catalytic tests were performed in an optimized (photo-)reactor operating at room temperature and atmospheric pressure. The GH-$MnFe_2O_4$/GDL electrode achieved an outstanding NH_3 yield of 7.3 ppm h^{-1} and Faradaic efficiency of 90% at -0.2 V vs. RHE in PEC systems, demonstrating significant potential as an alternative to the energy-intensive Haber-Bosch process for nitrogen reduction under ambient conditions.

Preferred and 2nd choice for the topic: Photocatalysis and photoelectrocatalytic approaches, solar energy utilization, Fundamental advances in understanding catalysis.

Oral preferred or Short Oral / Poster

Introduction and Motivations

Large-scale ammonia production relies predominantly on the Haber-Bosh process, which operates under severe conditions (400-600 °C and 20-40 MPa)[1]. In contrast, emerging technologies such as photocatalytic (PC), electrocatalytic (EC), and photoelectrocatalytic (PEC) methods offer promising pathways for more sustainable and decentralized NH_3 production[2]. The efficiency of these processes depends critically on factors like the electronic structure, material composition, semiconductor morphology, and the separation efficiency of photoinduced charge carriers. Spinel ferrites (MFe_2O_4 where M = Fe, Co, Ni, Mg, Mn, Cu, Zn) have garnered attention due to their unique optical properties –narrowed band gaps and enhanced visible light absorption– attributed to the d-d transitions influenced by oxygen ligand arrangements around Fe ions. Furthermore, substrate porosity plays a crucial role in facilitating N_2 reduction to NH_3.

Materials and Methods

Graphene (GH)-manganese ferrite ($MnFe_2O_4$) was synthesized by dissolving $MnCl_2{\cdot}6H_2O$ and $FeCl_3{\cdot}6H_2O$ salts in 100 mL of water enriched with Natural Organic Matter (NOM). The pH was adjusted to 0.5 using a 5 M HCl aqueous solution, followed by the addition of graphite. The mixture was basified to a pH of 10.5, dried at 100 °C for 48 h, washed with deionized water, and redried at 60 °C for 72 h. $MnFe_2O_4$ catalyst was synthesized using the same methodology without graphite dispersion. The catalysts were deposited on GDLs via drop-coating method. For this, 10 mg of powder, 500 µL of isopropanol and 500 µL of water were mixed and sonicated for 1 h. The resulting ink was uniformly deposited on the GDL surface (loading: 1 mg cm^{-2}) and then dried at room temperature. Commercial GDL substrates with different porosity were used to study the influence of diffusion phenomena on catalytic reactivity.

Nitrogen reduction tests were performed at ambient conditions in a custom three-electrode flow electrochemical cell equipped with a quartz window[3]. Ammonia was quantified by ion chromatography (IC) and UV-Vis spectrophotometry[4].

Results and Discussion

Figure 1a compares the PEC performance of $MnFe_2O_4$/GDL and GH-$MnFe_2O_4$/GDL electrodes under applied potentials ranging from -0.2 V to -0.6 V vs. RHE. For the $MnFe_2O_4$/GDL electrode, NH_3 production increases with applied potential, reaching a maximum of around 3 ppm at -0.4 V. The Faradaic Efficiency (FE) is higher at low voltage, and then decreases significantly with the applied potential, dropping from 36% at -0.2 V to 0.11% at -0.6 V. In contrast, the GH-$MnFe_2O_4$/GDL electrode, incorporating graphene into its structure, exhibits superior performance. At -0.2 V, it achieves an NH_3 concentration of 7.3 ppm, with an outstanding FE of 90% at -0.2 V. As illustrated in Figure 1b, the NH_3 formation rates are quite different across the three reduction processes, i.e. PC, EC, and PEC. The highest performance is observed with the GH-$MnFe_2O_4$/GDL when this electrode is used as photo-electrode in a PEC apparatus. This higher efficiency was due to the adsorption capacity of the N_2 molecule on semiconductors containing empty or half-filled *d* orbitals, such as the manganese ions present in the GH-$MnFe_2O_4$ structure.

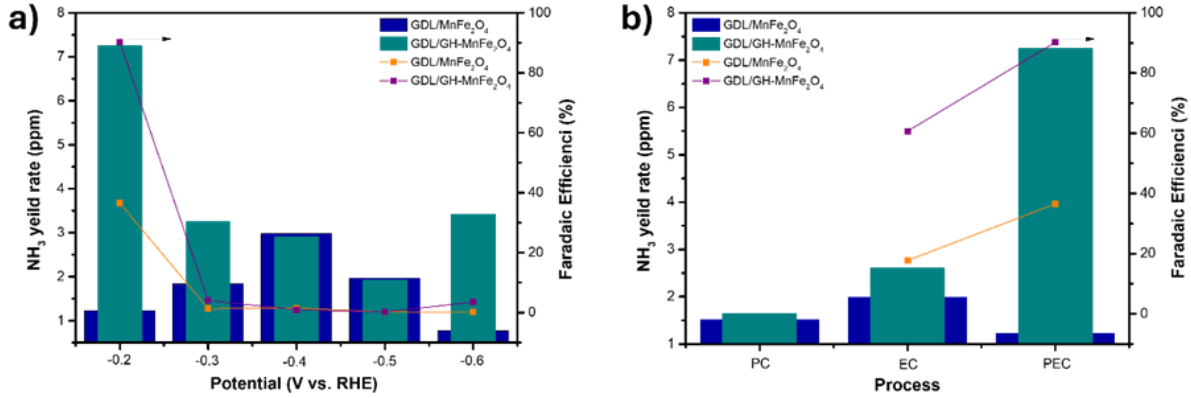


Figure 1 a) Production of NH_3 for $MnFe_2O_4$/GDL and GH-$MnFe_2O_4$/GDL electrodes a) at different applied potentials and b) with different catalytic approaches (photo-catalytic -PC, electro-catalytic -EC, and photo-electro-catalytic -PEC).

The influence of substrate porosity was also investigated by testing different GDLs with varying pore size to enhance diffusion properties and overcome the issue of low N_2 solubility in aqueous media. Results demonstrate that substrate porosity plays a critical role NH_3 production, with higher porosity leading to increased NH_3 production rate.

References

1. C. Ampelli, *Nature Catalysis* **2020**, *3*, 420-421.
2. G. Centi, C. Ampelli, *Journal of Energy Chemistry* **2024**, *91*, 680-683.
3. V. Longo, L. De Pasquale, F. Tavella, M. Barawi, M. Gomez-Mendoza, V. de la Peña O´Shea, C. Ampelli, S. Perathoner, G. Centi, C. Genovese, *EES Catalysis* **2024**, *2*, 1164-1175.
4. F. Tavella, D. Giusi, C. Ampelli, *Current Opinion in Green and Sustainable Chemistry*, **2022**, *35*, 100604.

Acknowledgements

This work is funded by Coordination for the Improvement of Higher Education Personnel (CAPES, Finance Code 001; grant 88887136426/2017/00) and by the Italian Ministry for Universities and Research (MUR) through the PRIN Project HYDREAM (2022YXHXH5ID), which are gratefully acknowledged. The authors are also grateful to FAPESP.

Plasma-assisted electrochemical conversion of nitrogen to ammonia under ambient conditions

Marco Francesco TORRE[*,1], Lavanya VEERAPURAM[1], Francesco TAVELLA[1], Siglinda PERATHONER[1], Gabriele CENTI[1], Chiara GENOVESE[1], Claudio AMPELLI[1]

[1] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences (ChiBioFarAm) – University of Messina, ERIC aisbl and CASPE/INSTM, V.le F.Stagno d'Alcontres, 31 – 98166 Messina, Italy*

** marco.torre1@studenti.unime.it*

Significance and Relevance

This study introduces an innovative aqueous plasma electrolytic device utilizing a micro-plasma cathode for direct ammonia synthesis under ambient conditions, starting from gaseous dinitrogen (N_2) and water. Ammonia (NH_3) is produced via solvated electrons generated by plasma, eliminating the need for additional reagents or catalytic materials. We present here the optimization of this plasma electrolytic system through the adjustment of key operational parameters, highlighting its potential as a sustainable and efficient alternative for ammonia production.

Preferred and 2nd choice for the topic: Advanced process with electrocatalysis and plasma utilization, Catalysis to electrify the chemical production
Preferred presentation: Oral preferred or Short Oral / Poster

Introduction and Motivations

Ammonia is an essential chemical product for industry, powering the production of fertilizers, pharmaceuticals, and explosives. However, the traditional Haber-Bosch process used for NH_3 synthesis, while efficient, is resource-intensive, demanding significant energy and capital investment, and contributing heavily to greenhouse gas emissions.[1]
Plasma catalysis has emerged as a promising innovation in catalytic technology, offering a sustainable alternative to traditional industrial processes.[2] When powered by renewable energy sources like wind or solar, plasma catalysis has the potential to drive the electrification of the chemical industry, drastically reducing its environmental footprint. In this work, we integrated a non-thermal plasma microjet into an electrochemical cell. The microjet, acting as a cathode, interacts with an aqueous electrolytic solution, generating radical species that catalyse the formation of NH_3, and hydrogen (H_2) as the primary side product. The optimization of the key operational parameters is critical to enhancing plasma microjet's performance and maximizing NH_3 production efficiency.

Materials and Methods

The plasma-electrolytic system designed for NH_3 synthesis consists of i) a glass reaction cell, sealed with a Teflon screw lid equipped with four openings for the passage of two gas tubes (inlet and outlet), ii) a stainless-steel capillary tube for plasma generation, and iii) a Pt electrode. The plasma microjet serves as the cathode, while the Pt electrode functions as the anode. Dinitrogen gas is continuously flowed through the capillary, positioned at a specific distance above the electrolytic solution. Upon applying a potential difference between the two electrodes, a plasma is generated inside the capillary, initiating the reaction. Figure 1a shows a representative scheme of the experimental apparatus.

Results and Discussion

The optimization of the plasma electrolytic device was performed by systematically varying key operational parameters, including the plasma-liquid surface gap (PLG), N_2 flow rate, capillary tube inner diameter (ID), and applied current. These adjustments significantly enhanced both the Faradaic Efficiency (FE%) and NH_3 production rate, achieving values of 70% and 0.23 mg h^{-1}, respectively, as illustrated in Figure 1b.

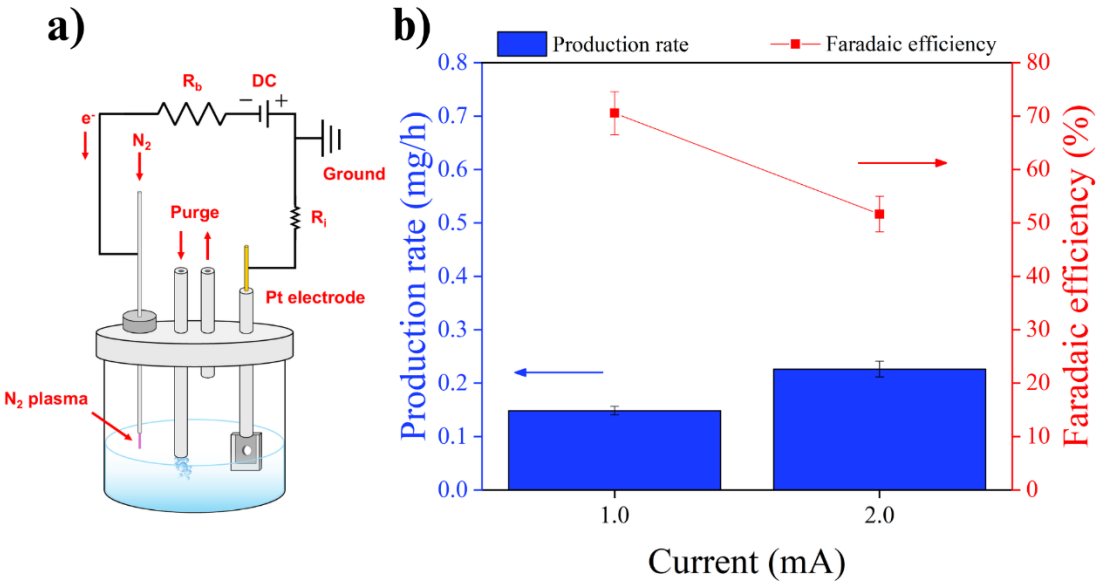


Figure 1) a) Plasma-electrolytic cell and b) ammonia production rate (mg h^{-1}) with corresponding FE%.

The challenge lies in maintaining both high NH_3 Faradaic selectivity and production rate when varying the other parameters, such as the current between the two electrodes. The reaction chemistry involves the reduction of protons (H^+) to NH_3 (and H_2), as well as the formation and reaction of H· radicals. Experiments performed at different pHs and using scavengers are under progress to provide deeper insights into the reaction mechanism.

However, the power consumption of the plasma electrolytic system is still larger than that of the Haber-Bosh process for NH_3 synthesis. Reducing these costs will require further optimization of reactor geometry and the evaluation of alternative electrode materials, but a fundamental understanding of the reaction mechanism remains crucial.

Although further investigation into additional setup parameters is necessary, these preliminary results highlight the potential of this plasma-assisted approach as a sustainable and efficient method for nitrogen fixation at ambient conditions, particularly for distributed small-scale NH_3 production.

References

1. F. Tavella, D. Giusi, C. Ampelli, *Curr. Opin. Green Sustainable Chem*. **2022**, *35*, 100604.
2. C. Ampelli, M.L. Carreon, Y. Liu, *J. Energy Chem*. **2024**, *99*, 300-301.

Acknowledgements

This work was funded by the European Union through the SUPERVAL (ID: 101115456) H2020 project by the Italian Ministry for Universities and Research (MUR) through the PRIN Project HYDREAM (2022YXHXH5ID), which are gratefully acknowledged. MFT acknowledges CASALE SA for co-funding his PhD grant.

Application of Manganese oxides support on Zeolite Y Catalysts in Benzene Total Oxidation

Xuerui ZHENG[1], Hisahiro EINAGA[*,2]
[1] *Department of Interdisciplinary Engineering Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka, Japan.*
[2] *Department of Material Sciences, Faculty of Engineering Sciences, Kyushu University, Kasuga, Fukuoka, Japan.*
** einaga.hisahiro.399@m.kyushu-u.ac.jp*

Significance and Relevance

In this study, we investigated the performance and structural evolution of Mn/Y catalysts in benzene ozonation, focusing on their redox states and regeneration potential. The Mn/Y catalysts exhibited high benzene ozonation rates at low temperatures. Unlike the results with amorphous SiO_2 supports, differences in manganese precursors did not significantly impact the catalytic activity on Y zeolite, likely due to the rapid reaction rate. Structural changes after benzene ozonation were attributed to interactions with intermediate products, whereas heat treatment at 500°C effectively restored the structure and activity of the catalyst.

Preferred and 2nd choice for the topic: Air cleaning and combustion; Fundamental advances in understanding catalysis.
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Volatile organic compounds (VOCs) such as benzene are hazardous pollutants, and their efficient removal is critical for environmental protection and public health[1]. Catalytic ozonation, which uses ozone as an oxidant, is a promising method for VOC degradation because it enables effective oxidation at relatively low temperatures[2]. Manganese oxides (MnO_X) have been widely studied in catalytic ozonation because of their strong redox capabilities, which generate reactive oxygen species that enhance VOC conversion to CO_2. Prior studies have shown that the Mn precursor can influence the oxidation state and dispersion of MnO_X supported on amorphous SiO_2, affecting the catalytic performance. However, the effects of different types of Mn precursors on catalytic activity, particularly on the zeolite Y carrier, are not yet fully understood. This study aimed to clarify these effects by exploring both the catalytic performance and structural changes of Mn/Y catalysts during benzene ozonation, focusing on the mechanisms of catalyst deactivation and regeneration.

Materials and Methods

Manganese oxides were supported on zeolite Y (Mn/Y) catalysts via a dry impregnation method using aqueous solutions of $Mn(CH_3COO)_2{\cdot}4H_2O$ and $Mn(NO_3)_2{\cdot}6H_2O$. The zeolite Y support was supplied by JGC Catalysts and Chemicals Ltd. The manganese oxide loading was 5 wt%. The samples were then calcined at 500 °C for 3 h in air. The catalysts prepared from manganese acetate and nitrate are denoted by Mn/Y-a and Mn/Y-n, respectively.

Benzene ozonation reactions were performed in a fixed-bed reactor at atmospheric pressure. The reactor was loaded with 25 mg of the catalyst. Catalytic benzene ozonation was performed with an inlet O_3 (1700 ppm) and benzene (150 ppm) were fed into the reactor at a total gas flow rate of 1000 $mL{\cdot}min^{-1}$. Ozone was generated using a corona discharge generator. Prior to the reaction, the catalyst was activated at 450 °C in the O_2 flow for an hour.

The samples are labeled as follows: fr-a and fr-n for fresh catalysts; O_3-a and O_3-n after exposure to 2400 ppm ozone for 1 h; af-a and af-n after benzene ozonation for 1 h; and 200-a, 300-a, 400-a, and 500-a (and -n) after heat treatment at 200°C, 300°C, 400°C, and 500°C, respectively.

Results and Discussion

Figure 1 shows the XANES spectra of Mn/Y catalysts. The average oxide state (AOS) of Mn/Y-a, estimated from the absorption edge was between those of Mn(II) and Mn(III), with no shoulder peaks,

likely due to the high dispersion of manganese oxides on Mn/Y-a. This will be further investigated using EXAFS. After ozone decomposition, both catalysts (O_3-a and O_3-n) showed oxidation driven by O^{2-} formation from O_3; however, some O^{2-} was resistant to desorption, thereby inducing Mn oxidation. Benzene ozonation caused both Mn/Y-a and -n to reduce to Mn(II) due to highly reducing intermediates, as confirmed by in situ FTIR. Heat treatments restored the catalysts, with higher temperatures achieving conditions closer to those of the fresh catalysts.

As shown in **Figure 2**, fresh Mn/Y-a exhibited lower Mn-Mn peak intensity, indicating highly dispersed Mn oxides on zeolite Y. After O_3 exposure, the increased peak intensity indicated a reduction in defects as active oxygen species filled the vacancies. Benzene ozonation resulted in a single Mn-O peak at 1.7 Å, while ozone decomposition alone produced Mn-O (1.5 Å) and Mn-Mn (2.4 Å) peaks, revealing that intermediates from benzene ozonation caused MnO_X structural rearrangement. EXAFS results after heat treatment in O_2-N_2 also indicated that the heat treatment partially restored the Mn phase.

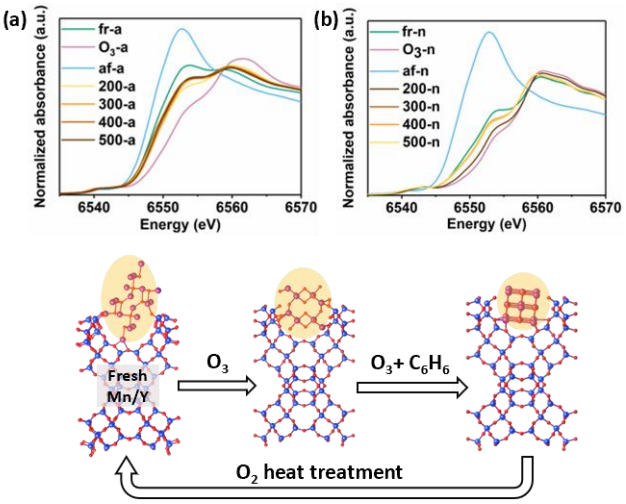


Figure 1 XANES spectra. (**a**) Mn/Y-a, (**b**) Mn/Y-n

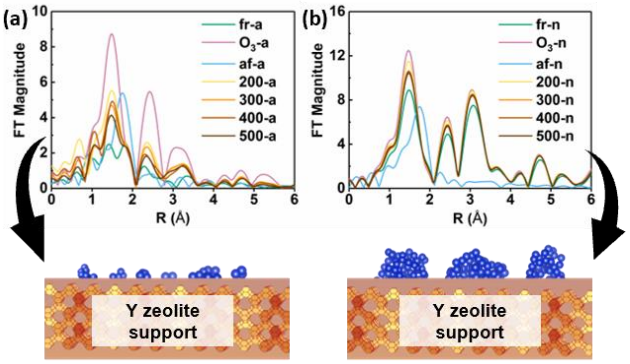


Figure 2 EXAFS signals. (**a**) Mn/Y-a, (**b**) Mn/Y-n

Figure 3 compared the catalytic activities of the Mn/Y catalysts with those reported previously[3,4,5]. The Mn/Y catalyst exhibited excellent benzene oxidation and CO_2 selectivity. Highly dispersed Mn/SiO_2-a exhibited a benzene oxidation rate approximately 1.5 times higher than that of the aggregated Mn/SiO_2-n. However, for the Mn/Y catalysts, the reaction rates remained high and the differences were not significant.

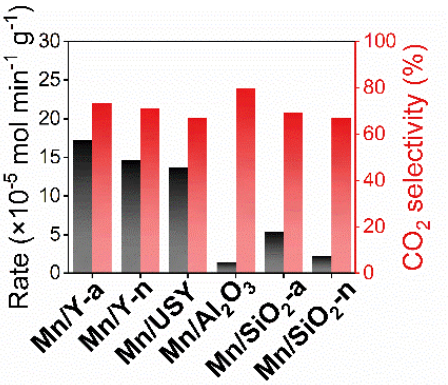


Figure 3 Benzene ozonation at 70°C

References

1. A. Mozaffar, Y.L. Zhang, *Curr. Pollut. Rep.* **2020**, *6*, 250–263.
2. B. Liu, H. Huang, *J. Hazard. Mater.* **2022**, *422*, 126847.
3. H. Einaga, *J. Catal*. **2013**, *305*,227–237.
4. H. Einaga, *J. Catal*. **2006**, *243*,446–450.
5. H. Einaga, *Catal. Today*. **2015**, *242*,287–293.

Acknowledgements

This work was financially supported by JST A-STEP program (JPMJTR20TE), JST SICORP program (JPMJSC18H3), and JSPS KAKENHI Grant Number 21H03635.

Uniform SiO_2@CeO_2 core-shell structures doped with CuO and Co_3O_4 as efficient catalysts for toluene combustion

Magdalena ŻUROWSKA*[,1,2], Anna ROKICIŃSKA[1], Dominika WAŚNIOWSKA[1], Marek DĘBOSZ[1], Piotr KUŚTROWSKI[1]
[1] *Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, Kraków, Poland.*
[2] *Doctoral School of Exact and Natural Sciences, Jagiellonian University, Łojasiewicza 11, Kraków, Poland.*
** magda.zurowska@doctoral.uj.edu.pl*

Significance and Relevance

Finding optimal catalysts for the total oxidation of volatile organic compounds (VOCs) is currently a significant challenge due to an increasing level of air pollution and threats related to the VOCs emission. Oxide systems can be successfully used in this process but they have to be optimally designed in terms of composition and distribution of both active phase and support. The presented work shows the potential of materials based on the synergy between the CuO, Co_3O_4 and CeO_2 phases arranged in one catalytic bed working in the toluene combustion.

Preferred and 2nd choice for the topic: Air cleaning and combustion, Automotive and stationary emission control (2nd choice)
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

One of the most important challenges for environmental sustainability is to reduce the emission of harmful VOCs into the atmosphere. In light of the constantly tightening regulations, many technologies for effective removal of VOCs have been developed, including catalytic total oxidation over materials containing noble metals (e.g. Pt, Pd, Au, Ag) and transition metal oxides (e.g. CuO, MnO_2, Fe_2O_3, Co_3O_4). The transition metal oxide catalysts, despite their lower activity compared to noble metals, are much cheaper and more resistant to poisoning.[1] On the other hand, their lower catalytic activity can be partially compensated by a proper design of active phase support. For example, cerium(IV) oxide can be effectively used in this role. CeO_2 has attractive properties due to a large number of oxygen defects that favor an extraordinary capacity for storing and releasing oxygen. Furthermore, CeO_2 provides enhanced thermal stability and high dispersion of the active phase. Although ceria can act as a single-component catalyst in the VOCs combustion, its activity can be significantly improved by an introduction of transition metal oxides. In such a case, a synergistic effect appears due to the formation of redox pairs Ce^{4+}/Ce^{3+} and $Me^{n+}/Me^{(n-1)+}$ leading to enhanced oxygen mobility. In the presented work, CuO/CeO_2 and Co_3O_4/CeO_2 oxide systems were deposited on nanometric, non-porous SiO_2 spheres to form novel core-shell SiO_2@CeO_2/MeO_x (Me = Cu or Co) catalysts. Such a catalyst grain design allowed for better exposure of the active components of the material to the reaction mixture.[2] The catalytic performance of individual and variously mixed systems in the combustion of toluene, as a representative of aromatic VOCs, was discussed.

Materials and Methods

SiO_2 spheres were prepared using the Stöber strategy. To facilitate the deposition of a precursor of another oxide phase on the SiO_2 surface, it was initially modified by anchoring an aminosilane coupling agent, i.e. 3-aminopropyltriethoxysilane (APTES). A core-shell SiO_2@CeO_2 support structure was synthesized by precipitation of a CeO_2 precursor on the surface of a spherical silica scaffold at constant pH. Finally, the formed SiO_2@CeO_2 support was modified with transition metal oxide precursors using the wet impregnation method to obtain the Co or Cu content of 5, 10, and 15 wt.% in the final catalysts.

Extensive physicochemical characterization was performed for the synthesized catalysts in terms of their morphology (SEM-EDS), surface and bulk composition (XPS and XRF), textural parameters (N_2 adsorption), structure (XRD), chemical environment (UV-Vis-DR), and reducibility (H_2-TPR). Most importantly, the catalytic performance of the developed materials in the combustion of toluene was studied.

Results and Discussion

The SEM images of the SiO_2@CeO_2 support revealed the homogeneous distribution of the CeO_2 phase, allowing the formation of the uniform shell while minimizing the presence of small bulk CeO_2 aggregates in interparticle voids. Conversely, the materials after Co and Cu oxide deposition showed slight particle aggregation due to the formation of clusters of active phase species on the support surfaces. However, a consistent spherical shape with a smooth surface was maintained. The deposition of CeO_2 significantly altered mesoporosity of the material. Nevertheless, the subsequent introduction of the active phase affected porosity due to its penetration into the pores formed by the CeO_2 washcoat. The formation of CeO_2, CuO, and Co_3O_4 phases for both the support and the catalysts was confirmed by XRD measurements. The UV-Vis-DR spectrum of the support revealed an absorption band associated with electron transitions in CeO_2. The Co-containing catalysts exhibited two additional wide bands, indicating the presence of Co_3O_4 phase. Furthermore, all copper catalysts displayed a low intense band below 300 nm attributed to the charge transfer $O^{2-} \rightarrow Cu^{2+}$, validating the existence of small crystalline CuO particles.

The critical aspect of the study was evaluating the activity of the obtained SiO_2@CeO_2/MeO_x core-shell materials in total oxidation of toluene (Figure 1). It was proven that the introduction of CuO significantly lowers the initial temperature of the toluene conversion, while Co_3O_4 promotes superior catalytic performance at higher temperatures. Various arrangements of the bicomponent catalytic bed (containing both SiO_2@CeO_2/CuO and SiO_2@CeO_2/Co_3O_4 materials) were tested to ensure operation over a wide range of temperatures. The catalyst composition was mixed in two ways: (i) the Cu and Co-containing catalysts were homogenously mixed at various ratios, or (ii) the catalysts were arranged in layers.

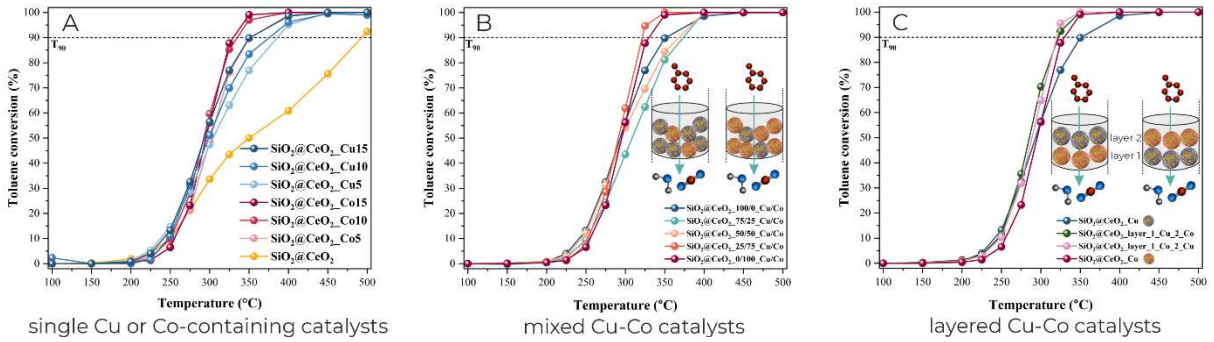


Figure 1. Catalytic activity in the toluene combustion of (A) single Co and Cu-containing, as well as (B) mixed Co-Cu and (C) layered Co-Cu catalysts.

The catalytic results confirm that the catalyst composition, including metal molar ratios, significantly influence the activity in the toluene combustion. The co-performance of the catalysts containing CuO and Co_3O_4 phases exhibits interesting correlations at their direct contact and separation. Furthermore, the stability tests of the developed catalysts in the toluene combustion were carried out at a specific temperature. The catalytic performance was tested alternatively in dry (1000 ppm of toluene in 100 ml/min of air) or wet atmosphere (1000 ppm of toluene in 100 ml/min of air saturated with 10 % vol. of H_2O). The developed systems demonstrated high stability, maintaining a high level of toluene conversion during 24 h measurements.

References

1. Y. Guo, M. Wen, G. Li, T. An, *Applied Catalysis B: Environmental* **2021**, *281*, 119447.
2. A. Rokicińska, P. Łątka, B. Olszański, M. Żurowska, M. Dębosz, M. Michalik, P. Kuśtrowski, *Chemical Engineering Journal* **2024**, *480*, 148173.

Acknowledgements

We thank the National Science Centre of Poland for financial support in the implementation of research (grant no. 2020/39/D/ST5/02703).

Enhancing Catalytic Activity through Manganese Addition in Co or Cu Mixed Oxides for catalytic treatment of wood combustion emissions

C.E. Bounoukta[1], C. Paris[1], M. Tannous[1], É. Genty[1], F. Devred[2], C. Poupin[1], S. Siffert[1], É. Gaigneaux[2], R. Cousin[1]
1 Unité de Chimie Environnementale et Interactions sur le Vivant (UCEIV UR 4492),
Université du Littoral Côte d'Opale, 145 avenue Maurice Schumann 59140 Dunkerque (France)
2 Institute of Condensed Matter and Nanosciences, Place Pasteur 1, L4.01.09, B-1348 Louvain-la-Neuve (Belgium)
**eric.genty @univ-littoral.fr*

Significance and Relevance

This study demonstrates that the combination of manganese with cobalt or copper in mixed oxide catalysts significantly enhances catalytic performance in both CO and toluene oxidation reactions. The synergistic effects between Mn and the transition metals (Co and Cu) lead to improved redox properties, higher surface area, and more efficient oxidation processes. These materials show promise for real-world applications where oxidation reactions need to be conducted at moderate temperatures, such as in environmental pollution control.

Topics: Air cleaning and combustion or Automotive and stationary emission control and Presentation preferred: *Oral only*

Introduction and Motivations

The biomass sector, and more specifically domestic wood heating, appears today to be a particularly promising alternative. In France, wood and biomass account for around 65% of renewable energy consumption for heat production. Thus, wood heating represents real challenges: energy issues for the environment and for public health. Nevertheless, wood energy is an integral part of the environmental issue. Emissions from wood combustion, both gaseous compounds and fine particles, are undeniably controversial. Among the pollutants produced by wood heating, several families can be distinguished: unburnt gases such as carbon monoxide (CO), Volatile Organic Compounds (VOCs), which include BTEX (Benzene, Toluene, Ethylbenzene and Xylene), and unburnt solid carbonaceous compounds [1].

Reducing these polluting emissions is crucial and requires the implementation of filtration and treatment technologies. Catalytic oxidation is known as one of the best solutions for reducing CO and VOCs. Total oxidation of CO at low temperature by transition metal oxides is a widely studied subject in heterogeneous catalysis [2,3]. Specifically, manganese oxides are interesting for toluene oxidation due to its availability and reactivity of surface oxygen species [3]. Transition metal oxides are also being studied as part of the total oxidation of VOCs and are very promising [3,4]. The use of LDH route for the synthesis of mixed oxides allows to develop some interesting properties for pollutants oxidation at low temperature, like high specific surface area and reducibility at low temperature.

To get as close as possible to the real conditions of wood combustion, this work is carried out on the simultaneous elimination of pollutants. Catalytic oxidation is one of the most effective methods for eliminating separately CO and VOCs, this is why it has also been chosen for treating mixtures of pollutants. The simultaneous catalytic oxidation of toluene and CO compounds in mixture has begun to be studied over the last decade, but the number of studies remains fairly limited [4]. In this work, we chose to study the activity of mixed oxides issued from LDH route. The main objective is to evaluate the influence for the association of Mn to Co or Cu-based catalysts for oxidation reactions of pollutants issued from the wood combustion (e.g. CO and toluene).

Materials and Methods

The synthesis method chosen to prepare LDH materials is classical co-precipitation with metal ratio M^{2+}/M^{3+} equal to 6/2. First, metal nitrates (Al, Mn, Co and/or Cu) are dispersed in 200 mL of distilled water. The solution is then added dropwise to a sodium carbonate solution (Na_2CO3). The pH is controlled throughout the addition, at around 9.5, by a sodium hydroxide solution (NaOH). Stirring is maintained at room temperature for 24 hours. Then, the solution is filtered and washed with hot demineralized water (60 °C), then dried in an oven at 60 °C for 24 hours. Finally, the powder obtained was thermal treated, up to 500 C for 4 hours under an air flow. For the trimetallic materials (MnCuAl and MnCoAl), the metal ratio

for Co (or Cu) /Mn is equal to 3/3. The catalysts prepared will hereafter be referred to as MnAl, CoAl, CuAl, MnCoAl and MnCuAl, it will be specified whether they are calcined or not.
The materials are characterized by XRD, XPS, N_2 sorption, H_2-TPR.
The toluene and CO mixture oxidation reactions were conducted at atmospheric pressure in a micro reactor containing 100 mg of catalyst. Catalytic tests were made using a gas mixture containing of 1000 ppm C_7H_8 and/or 1000ppm CO and 20% O_2 in He. The feed gases were analyzed by an Agilent 490 Micro gas chromatography and ADEV 4400 IR CO- CO_2 analyzer

Results and Discussion

Five different LDH materials were synthesized: CoAl, MnCoAl, MnAl, MnCuAl, and CuAl. These materials were first analyzed by X-ray diffraction (XRD) to confirm the presence of the LDH precursor phase. The characteristic diffraction peak of the LDH phase appeared at 2θ = 12°, confirming the presence of the layered structure in all precursor materials. Upon calcination at 500°C, the LDH phase fully decomposed, and the resulting mixed oxide phases were identified by XRD. Notably, the MnAl sample contained Mn_2O_3, Mn_3O_4, and the spinel phase $MnAl_2O_4$, while the CoAl sample showed Co_3O_4 and $CoAl_2O_4$. MnCuAl primarily showed the $MnAl_2O_4$ spinel phase, and CuAl exhibited only the CuO phase.

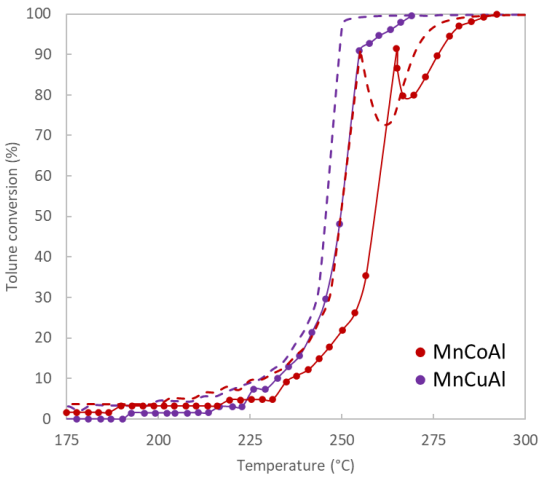


Figure 1 Conversion vs. temperature of toluene in presence or absence of CO

The catalytic performance of the mixed oxides was tested for CO oxidation. CoAl showed the highest activity, with 80% CO conversion at ambient temperature. However, when manganese was added to either Co or Cu (as in MnCoAl and MnCuAl), a significant improvement in catalytic performance was observed due to a synergistic effect.
For toluene oxidation, MnCuAl and MnCoAl exhibited significantly better activity than the individual components. The temperature for 50% toluene conversion (T_{50}) for MnCuAl and MnCoAl was below 260°C, whereas for CoAl, MnAl, and CuAl, the T_{50} values were higher, indicating lower catalytic activity. This synergy likely arises from the redox couples of Mn^{4+}/Mn^{3+} with Cu^{2+}/Cu^{+} (for MnCuAl) and Mn^{4+}/Mn^{3+} with Co^{3+}/Co^{2+} (for MnCoAl), which optimize the catalytic sites and enhance overall performance. A further experiment tested the effect of CO in a toluene/air gas mixture to simulate real-world catalytic conditions. The results showed that the presence of CO positively influenced the catalytic performance of both MnCuAl and MnCoAl, leading to better toluene conversion at lower temperatures. This improvement is likely due to the exothermic oxidation of CO, which generates localized heating on the catalyst surface, thus promoting the oxidation of toluene (Figure 1). The trimetallic samples (MnCuAl and MnCoAl) exhibited superior performance compared to the bimetallic samples due to this additional thermal effect. These materials show promise for real-world applications where oxidation reactions need to be conducted at moderate temperatures, such as in environmental pollution control.

References

[1] Y. Rogaume, *Pollut. Atmos.*, (2009) 27.
[2] M. Ghiassee, M. Rezaei, F. Meshkani, S. Mobini, *Environ. Sci. Pollut. Res.*, 28 (2021) 379.
[3] V. P. Santos, M. F. R. Pereira, J. J. M. Órfão, J. L. Figueiredo, *Appl. Catal. B Environ.*, 99 (2010) 353.
[4] E. Genty, J. Brunet, C. Poupin, S. Ojala, S. Siffert, R. Cousin, *Appl. Catal. B Environ.*, 247 (2019) 163.

Acknowledgements

The authors would like to express their gratitude to the region Hauts-de-France and the European Regional Development Fund (CPER “ECRIN” research project), ADEME (“Catacomb” project) and the PHC Tournesol (“Calmant” project) for their financial support of this research.

Comparative Study of SBA-15 and CNT Supports for Iron Catalysts in Fischer-Tropsch Synthesis

Thaieny ZUCOLOTTO*[,1], Martin SCHMAL[1], Anna ZIMINA[2], Jan-Dierk GRUNWALDT[2], Reinaldo GIUDICI[1]
[1]*University of São Paulo, Department of Chemical Engineering,*
Av. Prof. Luciano Gualberto, travessa 3, n. 380, São Paulo, Brazil.
[2] *Karlsruhe Institute of Technology, Department of Catalysis and Operando Spectroscopy, Hermann-von-Helmholtz-Platz - 76344, Karlsruhe, Germany.*
** thaieny-zucoloto@usp.br*

Significance and Relevance

This study highlights the impact of support materials on the performance of iron-based catalysts in Fischer-Tropsch synthesis (FTS). Fe/CNT outperformed Fe/SBA-15, achieving higher CO conversion (49% vs. 21%) and lower methane selectivity (27% vs. 52%). Notably, Fe/CNT favored long-chain hydrocarbons (C_5+ selectivity of 18%) over Fe/SBA-15 (7%). These results demonstrate the significant role of support in modulating catalytic activity and selectivity. The combination of advanced characterizations provides deeper insight into structure-activity/selectivity relationships, paving the way for rational design of more efficient FTS catalysts.

Preferred and 2nd choice for the topic:
Sustainable and clean energy production and transport
Fundamental advances in understanding catalysis
Preferred presentation: Poster

Introduction and Motivations

The goal to lower greenhouse gas emissions now and to overcome the impact on climate changes in future can be achieved exploiting the Power-to-Liquids (PtL) technology, especially in the hard to abate aviation sector. Sustainable aviation fuel (SAF) may be produced through Fischer-Tropsch synthesis (FTS), the conversion of synthesis gas into long-chain hydrocarbons using iron or cobalt-based FT catalysts[1-3]. The iron-based catalysts are an economically attractive alternative to the cobalt-based materials, their performance is strongly related to the structure of active site during the reaction. The chemical state and phase of iron and its interaction with support are the key parameters to understand the structure-activity relationship and the deactivation mechanism[4].

Results and Discussion

The performance of two iron-based catalysts, Fe/SBA-15 and Fe/CNT, during the FTS were studied focusing on how support material influences hydrocarbon selectivity and CO conversion. Both catalysts were synthesized using the deposition-precipitation method [5-6]. The SBA-15 mesoporous silica support was synthesized by USP laboratory and its structure was confirmed by X-ray diffraction (XRD), while commercially obtained multi-walled carbon nanotubes (MWCNTs) were functionalized by nitric acid treatment at 120°C for 6 hours to remove amorphous carbon and introduce surface functional groups. Hydrogen temperature-programmed reduction (H_2-TPR) analysis revealed three distinct Fe reduction peaks, indicating multiple stages of iron oxide reduction. Reduction temperatures were optimized for each support's stability and feasibility, with Fe/SBA-15 reduced at 650°C and Fe/CNT at 380°C, balancing thermal requirements with support tolerance.

FTS reactions were performed at 285°C, with a weight hourly space velocity (WHSV) of 3200 mL/h*gcat, under 20 bar pressure and a CO:H_2 ratio of 1:2. Pre-reaction characterization using Brunauer–Emmett–Teller (BET) surface area analysis, inductively coupled plasma (ICP) spectrometry, and X-ray absorption spectroscopy (XAS) provided detailed insights into catalyst composition and structural properties. Post-reaction X-ray photoelectron spectroscopy (XPS) offered crucial information on surface chemistry and iron oxidation states, with an emphasis on the formation of iron

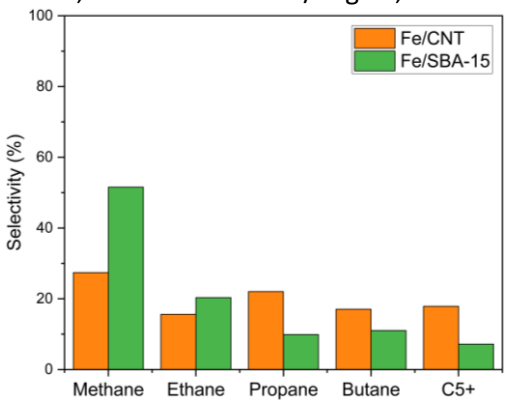
carbide structures, the active phase for FTS. This analysis helped elucidate the extent of iron carbide formation.

The results (Figure 1) showed a strong influence of support material on the catalytic performance of iron-based catalysts. Fe/CNT exhibited a higher CO conversion of 49%, compared to 21% for Fe/SBA-15, suggesting that the CNT support leads to a higher catalytic activity. Additionally, Fe/CNT demonstrated a lower methane selectivity of 27%, in contrast to a significantly higher methane selectivity of 52% for Fe/SBA-15. Selectivity towards C_5+ hydrocarbons was higher for Fe/CNT (18%) compared to Fe/SBA-15 (7%), suggesting that the CNT support favors the formation of long-chain hydrocarbons, while the SBA-15 support triggers more towards methane production.

These findings underscore the importance of support selection in tuning catalyst reducibility, stability, and hydrocarbon selectivity in Fischer-Tropsch synthesis, highlighting the advantages of mesoporous silica and carbon nanotube supports in influencing reaction pathways. This work enhances understanding of the role of support materials in iron-based catalyst performance, providing insights for developing tailored catalysts for efficient FTS and emphasized the importance of applying the combined characterization approach to enable the rational catalyst design.

Figure 1: Influence of support material on the catalytic performance of iron-based Fischer-Tropsch catalysts. Selectivity is categorized by hydrocarbon groups based on carbon number. Comparatively, SBA-15 support is shown to enhance methane production and restrict hydrocarbon chain growth.

Figure 1 – Comparison of hydrocarbon selectivity for CNT- and SBA-15 supported FTS catalyst (conditions: 285°C, WHSV at 3200 mL/h*gcat, 20 bar and 1CO:2H_2)



References

1. Moodley, D., Botha, T., Crous, R., Potgieter, J., Visagie, J., Walmsley, R. and Dwyer, C., Catalysis for a Sustainable Environment; John Wiley Sons, Ltd, **2024**; Chapter 6, pp 73–116.
2. Webb, P.and Filot, I., Comprehensive Inorganic Chemistry lll (third edition); Elsevier: Netherlands, **2023**; pp 354 – 380.
3. A. P. Raje and B. H. Davis, Catalysis Today,**1997**, 36, 335.
4. Kalz, K.F., Kraehnert, R., Dvoyashkin, M., Dittmeyer, R., Gläser, R., Krewer, U., Reuter, K. and Grunwaldt, J.D., ChemCatChem **2017**, 9, 17.
5. Bahome, M.C., Jewell, L.L., Hildebrandt, D., Glasser, D. and Coville, N.J., Applied Catalysis A: General; **2005**, pp 60-67.
6. Bellomi, S., Motta, D., Stucchi, M., Prati, L., Dimitratos, N. and Villa, A., Catalysts 14(2), **2024**, 119.

Acknowledgements

This study was financed, in part, by the São Paulo Research Foundation (FAPESP), Brasil. Process Number #2022/05469-6. Karlsruhe Institute of Technology (KIT) is acknowledged as host institution for Research Internships Abroad (BEPE-FAPESP), Process Number #2024/00852-1.

We acknowledge the financial support provided by CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) through Process 158797/2021-3.

Investigating Acidic Supports for Site-Selective Platinum Nanoparticles in VOC Oxidation

Alessia COMETTO[1*], Enrico Sartoretti[1], Nunzio Russo[1], Samir Bensaid[1].
[1]*Politecnico di Torino, Department of Applied Science and Technology (DISAT), Corso Duca degli Abruzzi 24, 10129 Turin, Italy.*
**alessia.cometto@polito.it*

Significance and Relevance

This study introduces a novel low-temperature catalytic approach for VOC oxidation, employing 3 nm Pt nanoparticles on ZSM-5 with varied Si/Al ratios, where acid sites enhance catalytic performance. The polyol reduction method enables precise nanoparticle size control, while a stirring-based loading technique prevents clustering, ensuring uniform dispersion. The catalyst achieves complete CO and VOC conversion at remarkably low temperatures (below 60 °C for CO and 90 °C for ethylene), demonstrating exceptional efficiency with promising applications in indoor air purification.

Preferred and 2nd choice for the topic: Air cleaning and combustion/Automotive and stationary emission control
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Volatile organic compounds (VOCs) are significant indoor air pollutants that pose serious health risks, underscoring the need for effective, low-temperature and sustainable removal strategies. Catalytic oxidation, especially using noble metals like platinum, has proven effective in VOCs abatement due to platinum's high oxygen activation efficiency. Due to the high cost of the metal, a low content of 0.5 wt% was selected. However, the catalytic performance of platinum is greatly influenced by interactions with acid sites in zeolite supports, such as ZSM-5. These interactions, along with the controlled dispersion and particle size of platinum nanoparticles, enhance the catalyst's activity and selectivity[1]. Strong acid sites in ZSM-5 promote VOCs adsorption and activation, which supports efficient oxidation. This study systematically explores how ZSM-5 acid sites affect the oxidation activity of size-controlled platinum nanoparticles, providing insights to advance low-temperature VOCs oxidation catalysts for indoor air quality improvement.

Materials and Methods

Platinum (Pt) nanoparticles were synthesized via polyol reduction method[1]. A NaOH solution in ethylene glycol (EG) was mixed with a platinum precursor, followed by stirring at RT for 1 h in inert atmosphere. The solution was then heated at 90°C to form a dark Pt colloidal suspension. The nanoparticles were precipitated with HCl, centrifuged, and stabilized with PVP. The deposition was performed on high surface area supports, including ZSM-5 zeolites with varying SiO_2/Al_2O_3 ratios (50, 80 and 117), and SBA-15 mesoporous silica as non-strong acid reference. Zeolites were pre-calcined to convert ammonium ions to protons. Two deposition methods, stirring and impregnation via solvent evaporation, were employed to achieve a low Pt content 0.5 wt%. The catalysts were then calcined and reduced in H_2. Before the test, samples were pre-treated at 110 °C in air flow. Catalytic oxidation was conducted in a fixed-bed quartz U-tube reactor, with a flow of 100 ppm pollutants in air (GHSV: 12.000-24.000 h^{-1}). The analysis was performed in isothermal steps. Characterization techniques included N_2 physisorption, XRD, NH_3-TPD, CO chemisorption, FESEM, TEM, EDX, and in-situ FT-IR analysis during deuterated acetonitrile chemisorption.

Results and Discussion

The N_2 physisorption analysis indicated that SBA-15 exhibits a higher surface area and pore size compared to ZSM-5, with no significant changes post-Pt deposition, preserving pore accessibility. The XRD patterns of the catalysts successfully confirmed the structural integrity and characteristic peaks of SBA-15 and ZSM-5 supports with no metallic platinum detected due to its low content (0.5 wt%) and excellent dispersion (60-90%), as confirmed by CO chemisorption[2]. EDX confirmed 0.4–0.5

wt% Pt loading, while TEM images revealed that the Pt nanoparticles in solution had controlled diameter of 2.7 nm, retaining a spherical shape. The stirring deposition maintained uniform dispersion (Figure 1.a)., while impregnation led to the formation of larger particle clusters[1] (Figure 1.b). NH_3-TPD analysis showed that ZSM-5 with lower Si/Al ratios contained a greater number and stronger acid sites, indicating that as the Si/Al ratio decreases, the number of acid sites in ZSM-5 generally increases in an approximately linear manner. Although SBA-15 only exhibited silanol groups classified as weak acids. Pt/SBA-15 sample showed the highest dispersion of platinum nanoparticles, likely due to its mesoporous structure and high surface area. This enhances the catalytic active surface, improving CO adsorption/activation ability of Pt species at low temperature, thereby effectively catalyzing the oxidation process. On the other hand, the Pt/ZSM-5 catalysts exhibit superior catalytic VOC oxidation performances. Brønsted acid sites play a crucial role in the oxidation of VOCs by acting as sites for protonation and activation of reactants, which facilitates the breaking of chemical bonds necessary for oxidation. The interaction between the acid sites and the metal can also promote better metal-support interaction, enhancing catalytic activity and stability (Figure 2)[3]. In this way, it is possible to achieve T_{90} temperatures for Pt/ZSM-5 catalysts via stirring below 75 °C. In conclusion, the results and excellent low-temperature performance provide a strong foundation for developing advanced indoor VOC mitigation and air purification systems.

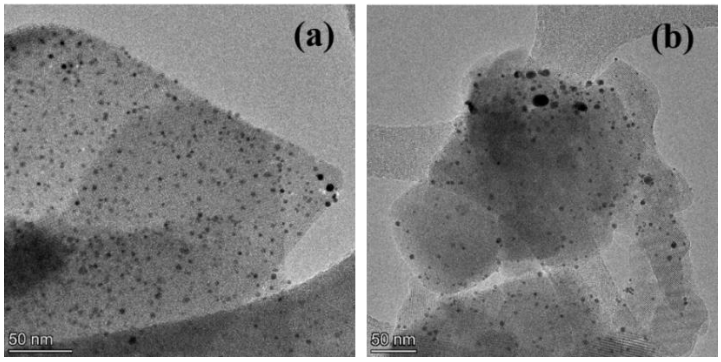


Figure 1. TEM images of (a) Pt/ZSM-5 (80) via stirring and (b) Pt/ZSM-5 (80) via impregnation with a scale bar of 50 nm.

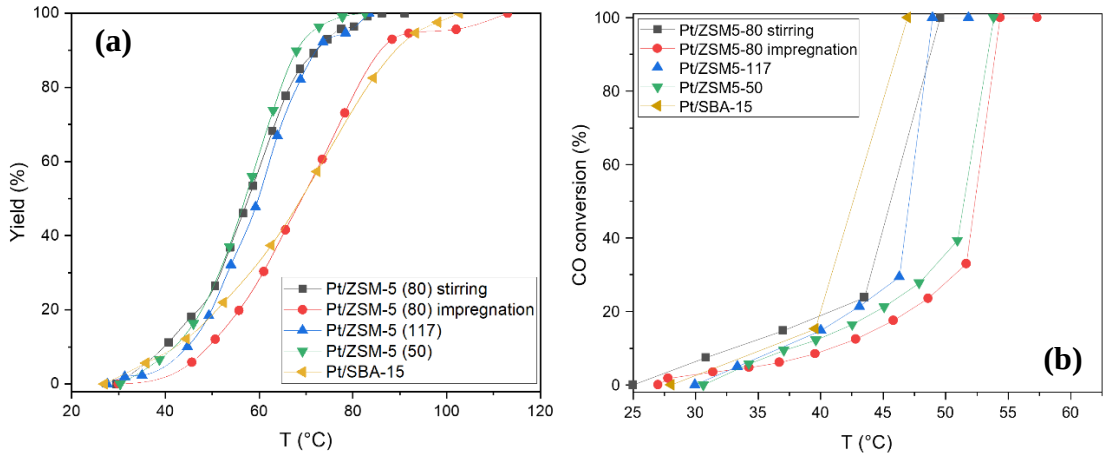


Figure 2. Catalytic oxidation of ethylene (a) and CO (b), over Pt/zeolite and Pt/silica catalysts. Gas feed conditions: flow= 50 mL/min, 100 ppm ethylene, 21 vol% O2, and N2 to balance. Temperature increases with steps in the 20-120 °C range.

References:

[1] C. Chen *et al.*, *Chem. Commun.*, 2015, vol. 51, fasc. 27, doi: 10.1039/C4CC09383F.
[2] N. An *et al.*, *J. Phys. Chem. C*, 2013, vol. 117, fasc. 41, doi: 10.1021/jp404266p.
[3] P. Treesukol *et al.*, *J. Phys. Chem. B*, 2005, vol. 109, fasc. 24, doi: 10.1021/jp0511348.

Acknowledgements

The REACT-EU program PON Ricerca e Innovazione 2014-2020 (D.M. 1062/2021) and the Italian Ministry of University and Research (MUR) are kindly acknowledged. This publication is part of the project PNRR-NGEU which has received funding from the MUR-DM 118/2023.

Impact of Cu/Mn ratio for CuMnOx prepared by oxalate coprecipitation : the essential point for total oxidation of model pollutants issued from biomass combustion

Julien Machinski[1], Eric Genty[1], Charf Eddine Bounoukta[1], Christophe Poupin[1], Valeria La Parola[2], Stéphane Siffert[1], Elise Berrier[3], Leonarda Francesca Liotta[2], Renaud Cousin[1]*

[1]*Unité de Chimie Environnementale et Interactions sur le Vivant (UCEiV), Université du Littoral Côte d'Opale (ULCO), Dunkerque, 59140, France*

[2]*Institute for the Study of Nanostructured Materials (ISMN)-CNR, Via Ugo La Malfa, 153, Palermo, 90146, Italy*

[3]*Unité de Catalyse et Chimie du Solide (UCCS), UMR 8181, Université de Lille, CNRS, Centrale Lille, Université Artois, Lille, 59000, France*

*renaud.cousin@univ-littoral.fr

Significance and Relevance

This study highlights the importance of Cu/Mn ratio on mixed oxides for the total oxidation of air pollutants application. The influence of this ratio was explored through various physicochemical characterization methods, notably revealing the presence of spinel phase ($Cu_{1.5}Mn_{1.5}O_4$) confirmed and a reducibility at lower temperature in presence of low content of Mn. Relations between catalytic activity and physicochemical properties were established, demonstrating that an optimal ratio enhances CO, toluene and black carbon oxidation at low temperatures, probably due to a synergistic effect between Mn_3O_4 and spinel phases.

Topics: Air cleaning and combustion or Automotive and stationary emission control and Presentation preferred: *Oral only*

Introduction and Motivations

The global shift towards renewable energy sources is reshaping the landscape of energy production, with biomass playing a pivotal role in this transition [1]. As a renewable and versatile fuel, biomass is increasingly favored; however, its combustion releases various pollutants, including carbon monoxide (CO), Volatile Organic Compounds (VOCs), Polycyclic Aromatic Hydrocarbons (PAHs), and soot particles [2]. These emissions pose significant environmental and health risks, underscoring the urgent need for effective remediation strategies.

Transition metal oxides present a cost-effective and efficient alternative to noble metal catalysts traditionally used for oxidation processes. Copper and manganese oxides are particularly promising due to their high activity for CO and VOCs total oxidation at relatively low temperatures [3-5]. Among the synthesis methods, oxalate co-precipitation offers a robust approach to producing mixed-metal oxide. This method not only enables co-precipitation of multiple metals into a single oxalate matrix but also results into small crystallite sizes for the mixed oxide phases, excellent reproducibility and low synthesis duration [6]. These characteristics are essential for developing catalysts that achieve high oxidation efficiency with structural and performance stability. In this study, the main objectives are the development of CuMn mixed oxides catalysts for an application in model oxidation reactions representatives to emission of biomass combustion. The impact of Cu/Mn ratios into mixed oxides will be discussed on the presentation and relations between catalytic activity and physicochemical properties will also be highlighting.

Materials and Methods

Copper-manganese oxalate precursors were synthesized as follows: copper nitrate ($Cu(NO_3)_2{\cdot}3H_2O$) and manganese nitrate ($Mn(NO_3)_2{\cdot}4H_2O$) were dissolved in 200 mL of pure acetone. Separately, oxalic acid was also dissolved in 200 mL of acetone under identical stirring conditions. The nitrate solution was then added directly to the oxalic acid solution under vigorous stirring, allowing for rapid oxalate precipitation. The resulting mixture was stirred for an additional 30 minutes before filtering, washing with acetone, and drying at 60°C for 48 hours. The dried oxalate precursor was then calcined at 500°C for 4 hours with a 1°C/min heating rate under an air flow of 3 L/h. The calcined samples were named based on their Cu:Mn ratios: $Cu_1Mn_4O_x$ (1:4), $Cu_1Mn_1O_x$ (1:1),

$Cu_4Mn_1O_x$ (4:1), alongside pure copper oxide (CuO_x) and manganese oxide (MnO_x) reference samples synthesized under identical conditions.

These materials were characterized by several physicochemical methods: XRD, H_2-TPR, XPS, N_2 sorption, SEM, Raman, IR, and UV-visible spectroscopy. Carbon black oxidation tests, N330 Degussa was mechanically mixed with the catalyst (10% carbon black, 90% catalyst). This mixture was analyzed using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), coupled with mass spectrometer to quantify carbon black oxidation into CO_2. For CO and toluene oxidation tests, 100 mg of each catalyst was pre-treated by heating under an air flow at 150°C. The gas mixture for CO oxidation was prepared to obtain 1000 ppm of toluene or CO in air flow 100 mL/min. Outflow gases were analyzed using Agilent 490 Micro gas chromatography and ADEV 4400 IR CO-CO_2 analyzer.

Results and Discussion

The oxalate precipitation method proved advantageous for the preparation of copper-manganese oxides, revealing significant textural and physicochemical differences. XRD analysis of mixed oxides show the presence of spinel phase ($Cu_{1.5}Mn_{1.5}O_4$) formation suggesting an interesting distribution of copper and manganese species, confirmed by microscopy analysis. The presence of mixed oxides allows to reduce the material at low temperature compared to the single oxide issued from oxalate precursors.

For CO total oxidation tests (Figure 1), the catalysts demonstrated improved performance with higher manganese content. The copresence of Mn_3O_4 and spinel phases enhances the catalytic oxidation at low temperature suggesting a synergetic effect between these two phases for total oxidation of CO. Moreover, the presence of Cu and Mn species is necessary in order to enhance the performance compared to CuO_x and MnO_x samples. Similar conclusions were observed for toluene oxidation, suggesting strong catalytic potential in VOC total oxidation.

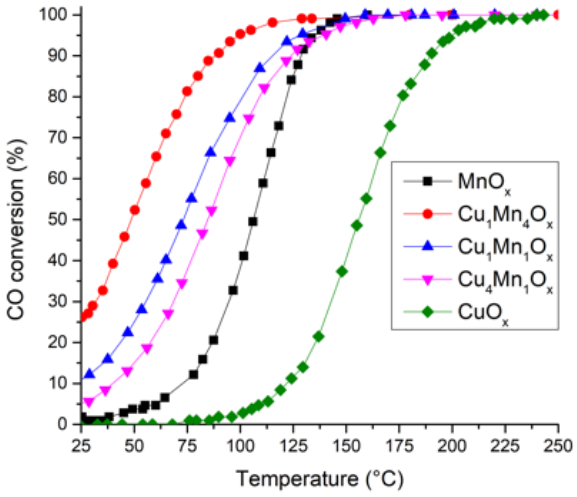


Figure 1. CO Conversion vs. temperature of $CuMnO_x$ mixed oxides

References

1. C. Paris, H. Dib, C. E. Bounoukta, E. Genty, C. Poupin, S. Siffert, R. Cousin, Catalysts. **2024**, 14(7), 455
2. R. Fan, J. Li, L. Chen, *et al.*, **2014,** *Environ. Res.*, *135*, 1–8.
3. R. El Khawaja, G. Rochard, E. Genty, C. Poupin, S. Siffert, R. Cousin, *Eur. J. Inorg. Chem*. **2023,** *26*(20), e202300213
4. M. Li, W. Zhang, X. Zhang, Y. Lian, X. Niu, Y. Zhu, *J. Colloid Interface Sci.* **2023**, *630*, 301-316
5. S. Dey, G. C. Dhal, D. Mohan, R. Prasad, *Mater. Discov.* **2018**, *12*, 63-71
6. Y. D. G. Edañol *et al.*, *IOP Conf. Ser.: Mater. Sci. Eng.* **2019**, *625*, 012016.

Acknowledgements

J. Machinski thanks the Région Hauts-de-France and the Pôle Métropolitain de la Côte d'Opale for his Ph.D. grant. The authors would like to express their gratitude to the region Hauts-de-France and the European Regional Development Fund (CPER "ECRIN" research project) and Interreg VI France-Wallonie-Vlaanderen ("CleanAirBouw" projet) for their financial support of this research.

Citrus Waste to Carbon Catalysts: A Sustainable Approach to CO_2 Reduction

Federica DE LUCA*,[1] Palmarita DEMORO,[1] Imen SGHAIER,[1] Izuchica NDUKA,[2] Rosa ARRIGO,[2] Siglinda PERATHONER,[1] Gabriele CENTI[1], Salvatore ABATE [1]

[1]ERIC aisbl and CASPE/INSTM, Dpt. ChiBioFarAM University of Messina Viale F. Stagno D'Alcontres 31, Messina, 98166, Italy
[2]School of Science, Engineering and Environment University of Salford M5 4WT, Manchester, UK

** e-mail federica.deluca@unime.it*

Significance and Relevance

This study explored the use of citrus waste as a sustainable and cost-effective precursor for CO_2 reduction electrocatalysts. Active Cu-based catalysts were successfully synthesized by leveraging the inherent reducing properties and porosity of citrus peels, particularly orange peels. The study revealed that the type of copper precursor and citrus peel significantly influenced the catalyst performance. Orange peel-derived catalysts, especially those prepared with sulfate precursors, exhibited superior activity and selectivity towards multi-electron reduction products like methane. This novel approach demonstrates the potential of waste biomass to contribute to sustainable energy solutions.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion/Advanced process with electrocatalysis and plasma utilization
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Within the framework of a circular economy, there exists the potential to enhance the economic value of waste materials, such as biomass, by repurposing them as precursors for carbon supports in electrocatalytic applications. Carbon derived from waste biomass offers a sustainable alternative due to its inherent renewability and low cost. The valorization of citrus waste provides a compelling case study for this approach. By investigating the utilization of citrus waste as a feedstock for the production of carbon-supported copper-based electrocatalysts, we have demonstrated its two-fold advantages: (i) it serves as the carbon support for copper nanoparticles (CuNPs), and (ii) it provides the reducing agents (e.g., ascorbic acid) necessary for the reduction of cationic copper species. This study aims to validate the feasibility of directly employing citrus waste in a one-pot synthesis of carbon-supported Cu nanoparticles and their subsequent application in CO_2 electroreduction.

Materials and Methods

Catalysts were synthesized via microwave-assisted hydrothermal treatment. A copper precursor ($CuSO_4$, $CuCl_2$, or $Cu(NO_3)_2$) was dissolved in distilled water at 50 °C. Finely ground orange or lemon peels were suspended in the copper precursor solution and further diluted with distilled water. The mixture was then subjected to microwave irradiation at 68 °C. The resulting catalysts were thermally annealed in an argon atmosphere at 500 °C, and characterized by XPS, SEM, XRD and TEM.

An ink was prepared by sonicating a mixture of the catalyst, Nafion, and absolute ethanol for 2 hours. This ink was subsequently deposited onto a gas diffusion layer (GDL) via spray coating. The resulting electrodes, serving as working electrodes, were evaluated using chronoamperometric detection in a three-electrode electrochemical cell. Experiments were conducted at two different potentials (-1.8 and -2 V vs. Ag/AgCl) in a 0.1 M $KHCO_3$ solution saturated with CO_2.

Results and Discussion

This work investigated the influence of copper precursors ($CuCl_2$, $Cu(NO_3)_2$, $CuSO_4$) and citrus peel type (orange, lemon) on the performance of C-supported Cu-based electrocatalysts for CO_2 reduction. While the copper precursor marginally affected the initial catalyst structure, it significantly impacted

the final carbon support structure. Sulfate-based precursors favored the formation of a more porous carbon structure, leading to enhanced CO_2 reduction, including multi-electron products such as CH_4. The type of citrus peel played a crucial role in catalyst performance. Orange peel-derived catalysts outperformed lemon peel-derived catalysts. Also, the redox properties of the peel constituents, particularly the higher reducing compounds present in orange peels, combined with the redox properties of the counter anions (Cl^-, NO_3^-, SO_4^{2-}), controlled the thermal restructuring of the peel. This process generated intrinsic porosity, more enhanced in the case of SO_4^{2-} anion, and facilitated the formation of Cu_2O/Cu core-shell nanoparticles also confirmed by XPS and TEM analysis. The resulting high porosity and strong reducing properties of orange peel-derived catalysts led to well-dispersed, stabilized Cu_2O/Cu nanoparticles, enhancing electrochemical surface area (ECSA) and promoting a diverse range of CO_2 reduction products, including CO, CH_4, and HCOOH. As reported in figure 1, the T-$CuSO_4$-O (sulfate precursor and orange peel) catalyst achieved the highest faradaic efficiency (FE) for both CO (12.8%) and CH_4 (4%) production at -2V Vs Ag/AgCl. In contrast, lemon peel-derived catalysts, with less favorable redox properties, exhibited poor nanoparticle stabilization and favored formic acid production, potentially due to excessive Cu exposure and hydrogen evolution reaction (HER).

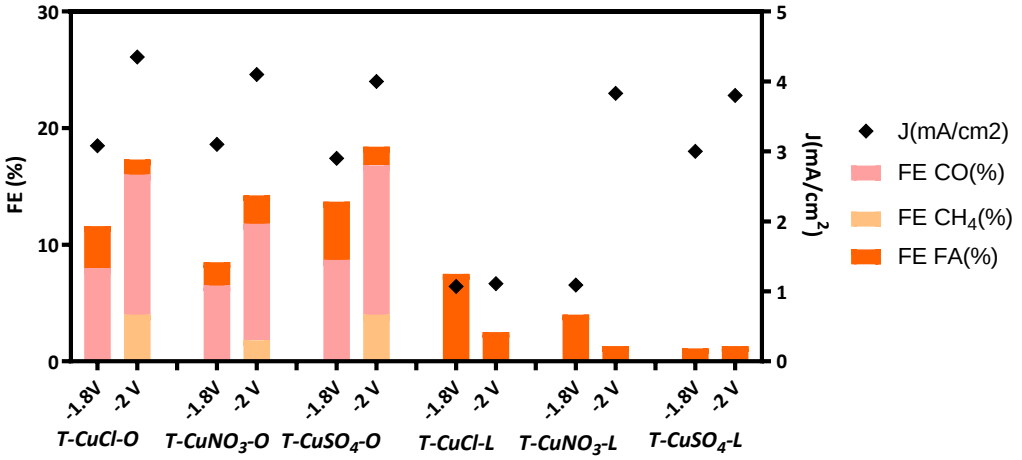


Figure 1: Current density (J), and faradaic efficiency of carbon monoxide (CO), formic acid (FA) and methane (CH_4) of orange peel-derived samples, and lemon peel derived samples after 1 hours of testing at an applied potential of -1.8 and -2 V vs Ag/AgCl.

These findings demonstrate the potential of valorizing citrus waste, particularly orange peels, as a sustainable and cost-effective precursor for efficient CO_2 reduction electrocatalysts. The insights gained from this study can guide the development of advanced electrocatalysts from various waste biomass sources for clean energy applications.

Acknowledgements

The project is funded by the ERC Grant “Surface-Confined Fast Modulated Plasma for Process and Energy Intensification" (SCOPE), Grant No. 810182

Rational optimisation of biomass-derived γ-valerolactone cascade synthesis

Alessandro ALLEGRI[1], Luca CIACCI[1], Fabrizio PASSARINI[1], Andrea BRIGLIADORI[2], Claudio OLDANI[3], Giuseppe FORNASARI[1], Stefania ALBONETTI[1]*

[1] *Alma Mater Studiorum – University of Bologna, Department of Industrial Chemistry "Toso Montanari", C3 – Center for Chemical Catalysis, CIRI-FRAME, Via P. Gobetti 85, Bologna, Italy.*

[2] *CNR-ISSMC (Former ISTEC), National Research Council of Italy-Institute of Science, Technology and Sustainability for Ceramics, Faenza, Italy.*

[3] *Syensqo, Bollate, Italy.*

** stefania.albonetti@unibo.it*

Significance and Relevance

This work presents a promising framework for tackling the development of complex processes, particularly for converting biomass-derived molecules into relevant products. A series of Aquivion/Zirconia (Aq/ZrO_2) composite catalysts were developed via spray freeze-drying (SFD), and then a Design-of-Experiment approach was employed to study the process parameters to identify optimal conditions to achieve conversion of biomass-derived furfuryl alcohol (FAL) into γ-valerolactone (GVL). This approach led to an increase in GVL productivity from 4'500 µmol h^{-1} g^{-1} to 18'000 µmol h^{-1} g^{-1}, demonstrating the potential of this approach.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion, Circular economy
Preferred presentation: Oral preferred

Introduction and Motivations

The development of biorefineries and the transition of the industrial landscape towards a future wherein fossil feedstocks are replaced with biomass-derived ones hinges on the invention and optimization of industrially relevant processes for the conversion of biomasses and biomass-derived feedstocks into desirable target products. Among such processes, the synthesis of γ-valerolactone (GVL) from biomass-derived feedstocks such as furfuryl alcohol (FAL) is of great interest for the potential application of the product in the production of chemicals, fuels and plastics.[1] This process involves a cascade reaction, the optimization of which requires proper tuning of multiple parameters, the interactions among which are not always predictable. The most common One-Variable-At-a-Time (OVAT) approach can elucidate the effect of the single parameters but is unable to provide insight into the interaction between different ones, if any. To overcome this limitation, Design-of-Experiment (DoE) can maximize information from the chemical data by variating the main parameters within their relevant ranges and enabling inferring a multivariate, data-driven regression model to predict the interaction of the different parameters within the desired domain. In addition, these goals are generally achievable with a lower number of experiments than OVAT.[2]
In this work, DoE was employed to rationalize the effect of five different parameters on the cascade synthesis of GVL. To carry out the reaction, Spray-Freeze Drying (SFD)[3] was employed to combine the Brønsted Acid Sites (BAS) of Aquivion and the Lewis Acid Sites of zirconia into bifunctional catalysts capable of converting FAL into GVL. Then, batch reactions were carried out following the experimental design to develop a data-driven model capable of predicting the effects of all five variables considered.

Materials and methods

High surface area zirconia was synthesized via precipitation at controlled pH, then was employed in conjunction with Aquivion water suspension (D79-25BS) for the SFD synthesis of the composite catalysts. The reactions were carried out in a batch reactor using FAL as a substrate and isopropanol as both solvent and hydrogen donor. The tests were carried out following a Face-Centered Design model with replicates wherein each parameter was normalized to three levels as reported in Table 1.

Table 1. DoE variables and levels

Level	Temperature (°C)	Time (h)	FAL Conc. (mmol L^{-1})	BAS/FAL (mol%)	Polymer Content (wt%)
1	180	3	200	1.5	30
0	165	2	133	1	20
-1	150	1	67	0.5	10

Results and Discussion

A set of 48 tests was defined and carried out in a random order to avoid systematic errors, investigating the effect that the five independent variables have on the catalytic performances, measured as both GVL productivity and selectivity. The obtained results were elaborated via MATLAB, building a quadratic regression model.

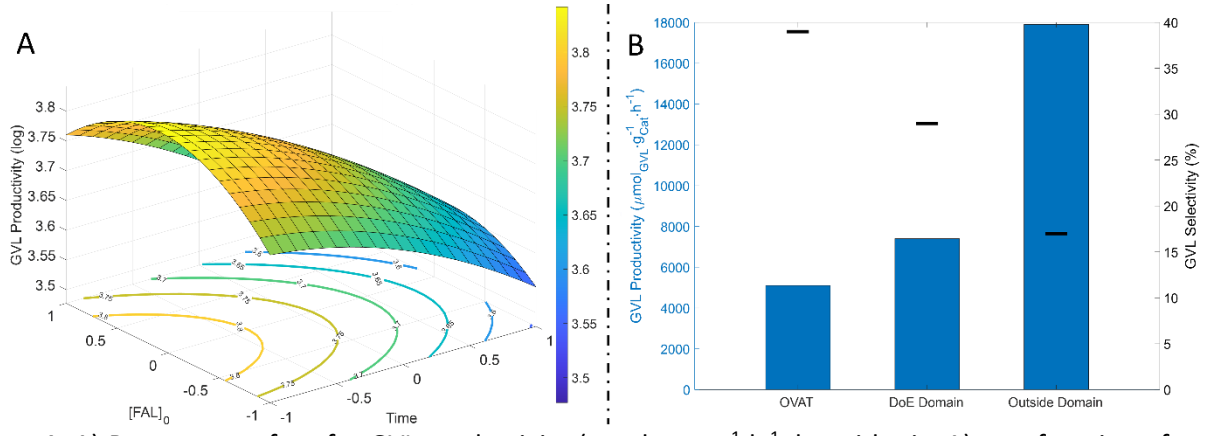


Figure 1. A) Response surface for GVL productivity ($\mu mol_{GVL}\ g_{Cat}^{-1}\ h^{-1}$, logarithmic, A) as a function of substrate concentration and reaction time. B) Results obtained from the investigation outside the experimental domain of the first DoE.

From the regression model, vast insight was gained on the behaviour of the system, especially on the interaction between the process variables. While reaction temperature showed the expected positive influence on both productivity and selectivity, reaction time showed a positive effect on selectivity and a negative effect on productivity (Figure 1A). More interestingly, the interactions between temperature and time, as well as between temperature and catalyst loading, were found to be negative. This is due to substrate degradation, which is more prominent when both reaction temperature and reaction time or catalytic loading are high.

While the regression model provided valuable insight into the behaviour of this complex system, it also indicated that maximization of catalytic performances would require an expansion of the experimental domain. Proper control of the interactions with other process parameters could allow further increase of the reaction temperature without causing excessive substrate degradation. Using the insight gained from the first study, new tests were carried out outside the initial experimental domain, increasing the reaction temperature, decreasing reaction time and keeping low catalytic loadings to prevent decomposition of molecules of interest. These tests yielded the result presented in Figure 1B; while the exploration of the initial experimental domain led to a 45% increase in GVL productivity over the initial OVAT studies, using the regression model as a guideline for further exploration increased productivity by a further 145% (corresponding to a 250% increase compared to the OVAT results).

References

1. A. Allegri et al., *ChemSusChem* **2024**, *17*, e202301683.
2. L. Ciacci et al., *J. Clean. Prod.* **2020**, 252, 119762.
3. C. Oldani et al., *Appl. Catal. A-Gen.* **2023**, 654, 119065.

A multiscale study of CH_4 pyrolysis over Fe-Al_2O_3 catalyst: the challenge of C build-up for the kinetic and the reactor studies

Marco ORSENIGO[1], Davide CAFARO[1], Veronica PIAZZA[1], Chiara NEGRI[1], Lidia CASTOLDI[1], Gianpiero GROPPI[1], Matteo MAESTRI[1], Alessandra BERETTA[*,1]

[1]*Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, Via La Masa, 34 – 20156 Milano, Italy.*

** alessandra.beretta@polimi.it*

Significance and Relevance

This work reports a multiscale study of CH_4 pyrolysis on iron catalyst, where the build-up of solid C challenges conventional studies in catalysis and calls for expert lab-scale and modelling methodologies. Tests were performed in thermobalance to identify promising catalyst formulations, in packed bed reactor to quantify kinetics, and in fluidized bed reactor to study the scaling of the process. Macroscale models with intrinsic kinetics and characterization of C-loaded solids (up to an unprecedented 4.5 g_C/g_{cat}) were applied to rationalize observed performance and optimize reactor operation.

Preferred and 2nd choice for the topic: H_2 storage and transportation, green H_2 production, hydrogen vectors; Multiscale modeling and advanced simulation aspects.
Preferred presentation: Oral preferred.

Introduction and Motivations

The thermo-catalytic reaction of CH_4 pyrolysis ($CH_4 \rightarrow 2\ H_2 + C(s)$, $\Delta H° = 75.6$kJ/mol) is receiving growing interest as source of CO_2-free hydrogen. Fe-based catalysts offer an advantageous balance in terms of cost, activity, resistance to deactivation, low toxicity and valuable carbon nanostructures[1]. However, the continuous build-up of carbon not only impacts catalyst performance during reaction, but also poses challenges for the kinetic analysis, reactor design and process scale-up. In this work, iron-based catalysts with Al_2O_3 as textural promoter were prepared and tested in CH_4 pyrolysis at different scales and reactor configurations, integrating experiments with a comprehensive reactor and kinetic modeling to guide process optimization and scale-up.

Materials and Methods

Fe-Al_2O_3 catalysts were prepared by fusion-decomposition method using nitrate salts. Tests on multiple scales were performed in three different lab-scale configurations: a thermobalance (TG, m_{cat}=5 mg), a packed bed reactor (PBR, m_{cat}=750 mg) and a fluidized bed reactor (FBR, m_{cat}=5 g). The effect of temperature (750-850°C), inlet CH_4 (10-95%), space velocity (1-20 NL/h/g_{cat}) and H_2 co-feed (0-80%) on catalyst activity and deactivation was investigated. Experiments were also designed to measure the C-load capacity of the catalyst.

Catalyst testing was coupled with a comprehensive characterization of the fresh, reduced and C-loaded catalyst, including microscopic (e.g., N_2 ads/des, XRD, FESEM, TEM, Raman) and macroscopic (e.g., measurement of density, particle size distribution, minimum fluidization velocity) properties.

Reactor models were developed to simulate experiments: a 1D dynamic reactor model for PBR was developed, able to describe the temporal evolution of the phenomena taking place along the axial coordinate of the reactor. FBR experiments were simulated with a dual modeling approach: Euler-Euler CFD numerical simulations, and Kunii and Levenspiel (KL) macroscopic model[2].

Results and Discussion

Reactive tests in thermobalance were performed on catalysts with different Fe loadings (12-97 wt%) to identify promising catalyst formulations: the catalyst with Fe:Al molar ratio of 50:50 demonstrated the optimal balance between Fe content and structural promotion by Al_2O_3.

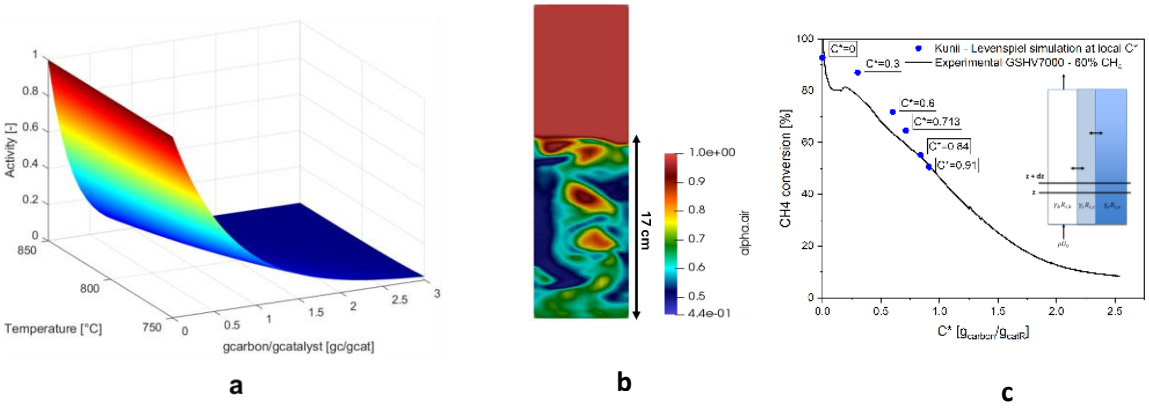
Tests in PBR were carried out to explore the effect of temperature, GHSV and feed composition on methane conversion and the corresponding C build-up curve ($C^* = g_C/g_{cat}$). In all tests, a rapid decrease

of conversion was observed, becoming progressively more pronounced at increasing methane feed content and temperature. The dynamic reactor model allowed to decouple and quantify the reaction and deactivation kinetics: the initial rate of methane decomposition (r^0, the reaction rate on the fresh C-free catalyst) was expressed with a first order dependence on CH_4 based on the extrapolation at zero *C** of conversion. An activity function (*a(t)*, defined as the ratio between *r(t)* and r^0) was then evaluated to account for the observed deactivation: this function establishes a quantitative correlation between the activity and the controlling parameters *C**, CH_4 partial pressure and temperature (Figure 1(a)).

Fluidization measurements and CFD analyses (Figure 1(b)) on fresh and C-loaded catalysts guided the design of experiments in FBR: minimum fluidization velocity and bed expansion were evaluated at increasing C*, and the existence of a bubbling fluidization regime was verified. A wide experimental campaign highlighted trends in line with those observed in PBR. Furthermore, the characterization of unloaded catalyst showed drastic changes of solid properties taking place during the evolution of C build-up: for instance, the bulk density decreased from 700 to 200 kg/m^3, accompanied by changes in particle size distribution and void fraction.

A KL macroscale model was developed, with the incorporation of the intrinsic kinetics and the detailed characterization of the C-loaded solids: this model showed good agreement with experimental data (Figure 1(c)), validating the approach and opening to further process optimization.

The further scale-up of this process requires advancements in catalyst shaping to ensure its suitability for fluidization, as well as dynamic modeling of the FBR. Both topics are currently under investigation. An additional challenge lies in carbon valorization: different potential applications are under evaluation (e.g., C-carrier for CO_2 storage, C as reducing agent), coupling the characterization and testing of unloaded catalyst with process analysis to assess the overall feasibility.



a **b** **c**

Figure 1: (a) Surface map of catalyst activity; (b) Euler-Euler simulation of a catalyst with C-load of 2 g_C/g_{Cat}; (c) Comparison between experiment in FBR and macroscopic model predictions.

In conclusion, this study investigates CH_4 pyrolysis on Fe-Al_2O_3 catalyst, combining tests across multiple scales, kinetic modelling and reactor modelling. Models and experience can now be transferred at larger scale testing and process analysis.

References

1. J.L. Pinilla, R. Utrilla, M.J. Lázaro, R. Moliner, I. Suelves, A.B. García, Fuel Process. Technol. 92 (2011) 1480-1488
2. Daizo Kunii & Octave, L. Fluidization Engineering. (1991)

Combining ab-initio thermodynamics and kinetics toward the Oxygen Evolution and Reduction Mechanism on a Dual Atom Catalyst

Elisabetta INICO[1], Giovanni DI LIBERTO[1], Gianfranco PACCHIONI[1]
[1]*Università degli Studi di Milano-Bicocca, Dipartimento di Scienza dei Materiali, Via R. Cozzi 55, 20125 Milano, Italy.*
** elisabetta.inico@unimib.it*

Significance and Relevance

We modeled a Dual Atom Catalyst for oxygen evolution and oxygen reduction reaction recently synthesized. Dual atom catalysts are now emerging for energy transition reactions such as water splitting. Starting from experimental data on the structure and electrochemical activity, we combined ab-initio thermodynamics and kinetics within density functional theory and combined it with the generalized Butler-Volmer formalism to understand the actual reaction mechanism.

Preferred and 2nd choice for the topic: Multiscale modeling and advanced simulation aspects
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Single Atom Catalysts (SACs) consist of isolated metal atoms stabilized on a support, maximizing the exposed active sites and showing behaviors that are reminiscent of coordination compounds[1,2] and are now widely investigated for catalytic approaches for the energy transition. Dual Atom Catalysts (DACs) are emerging as a promising frontier due to the possibility to use to catalytic centers. Starting from experimental results of the dual atom FeCo-N_3O_3@C[3], of which the structure is known, we investigate the reaction pathways for Oxygen Evolution and Oxygen Reduction Reactions (OER and ORR), providing evidence of the actual reaction mechanism which involves unconventional intermediates, that can form on single atoms.[4]

Results and Discussion

DFT calculations were conducted to simulate the Oxygen Evolution and the Oxygen Reduction on FeCo-N_3O_3@C (structure in Figure 1a). The ab initio thermodynamic approach including kinetic effects was combined with the generalized Butler-Volmer model.
Previous studies reported that on single atom catalysts OER does not follow the classical four-electrons step mechanism,[5] as alternative pathways are possible due to the formation of unconventional intermediates *OH*OH, *OH*O and O_2*.[4] In the case of DACs the picture is rather more complex due the very high number of possible adsorption configurations.

We observed that, in order to explaining the experimental results, oxygen evolution and oxygen reduction follow the same pathway. Looking the reaction in the OER direction, *OH must form on the Fe atom, and then the intermediates evolve on a bridging configuration between iron and cobalt. The adsorption of species on the cobalt site would lead to too strongly intermediated, that would poison the catalyst. The reason why the Co site does not take part in the reaction, although it is more reactive, is that it is strongly coordinated with solvent molecule. The ORR proceed similarly but in the opposite direction. Figure 1 reports a comparison between calculated and experimental polarization curves and the corresponding ORR pathway (panel b, c).

This study provides an example of the potential combination of the structural information with atomistic details, quantum chemical calculations, and activity experiments to understand the complexity of the reactivity of Dual Atom Catalysts.

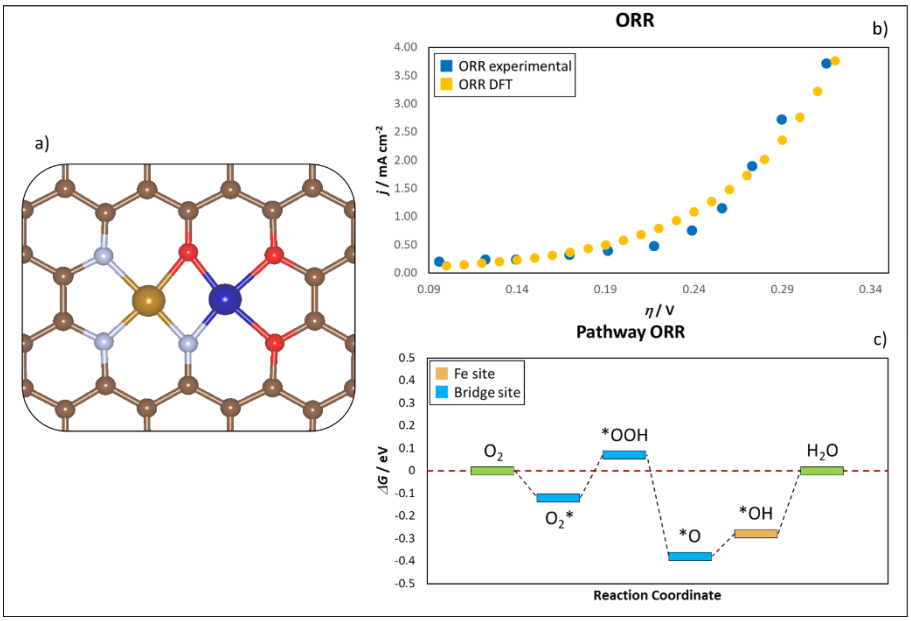


Figure 1: a) optimized structure of the FeCo-N_3O_3@C DAC. Color scheme: iron atom in gold, cobalt in blue, nitrogen in grey, oxygen in red and carbon in brown. b) polarization curves for oxygen reduction reaction. In blue the experimental curve is reported,[3] in yellow the simulated one. In panel c) the proposed pathway relative to the ORR curve in panel b) is reported.

References

1. A. Wang, J. Li, and T. Zhang, *Nat Rev Chem*, **2**, 65–81 (2018).
2. N. Cheng et al., *Nat Commun*, **7** (2016).
3. B. Tang et al., *Nature Synthesis*, **3**, 878–890 (2024).
4. I. Barlocco, L. A. Cipriano, G. Di Liberto, and G. Pacchioni, *J Catal*, **417**, 351–359 (2023).
5. R. R. Rao et al., *Energy Environ Sci*, **10**, 2626–2637 (2017).

DLP 3D printing of catalyst architectures: from material preparation to mathematical modeling of structure effects on catalyst performance

Luca MASTROIANNI*[1,2], Ananias MEDINA[2], Anna DE DOMENICO[1,2], Kari ERÄNEN[2], Martino DI SERIO[1], Dmitry MURZIN[2], Vincenzo RUSSO[1,2], Tapio SALMI[1,2]

[1]*Università di Napoli 'Federico II', Chemical Sciences, IT-80125 Napoli, Italy*
[2]*Åbo Akademi, Laboratory of Industrial Chemistry and Reaction Engineering (TKR), FI-20500 Turku/Åbo, Finland*
**luca.mastroianni@abo.fi*

Significance and Relevance

The potential of the high resolution Digital Light Processing (DLP) printing was exploited to create a new procedure for the design of catalyst structures with high geometrical complexity. The printed aluminum oxide catalyst structures had a good surface area combined with a sufficient mechanical strength. Ethanol dehydration experiments revealed a strong impact of the selected geometry on the catalyst performance, which was accurately described with an advanced heterogeneous mathematical model. Enormous potential of the developed shaping technique in process intensification is forecasted.

Preferred and 2nd choice for the topic: Multiscale modeling and advanced simulation aspects, CO_2 utilization and recycling
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster) Oral

Introduction and Motivations

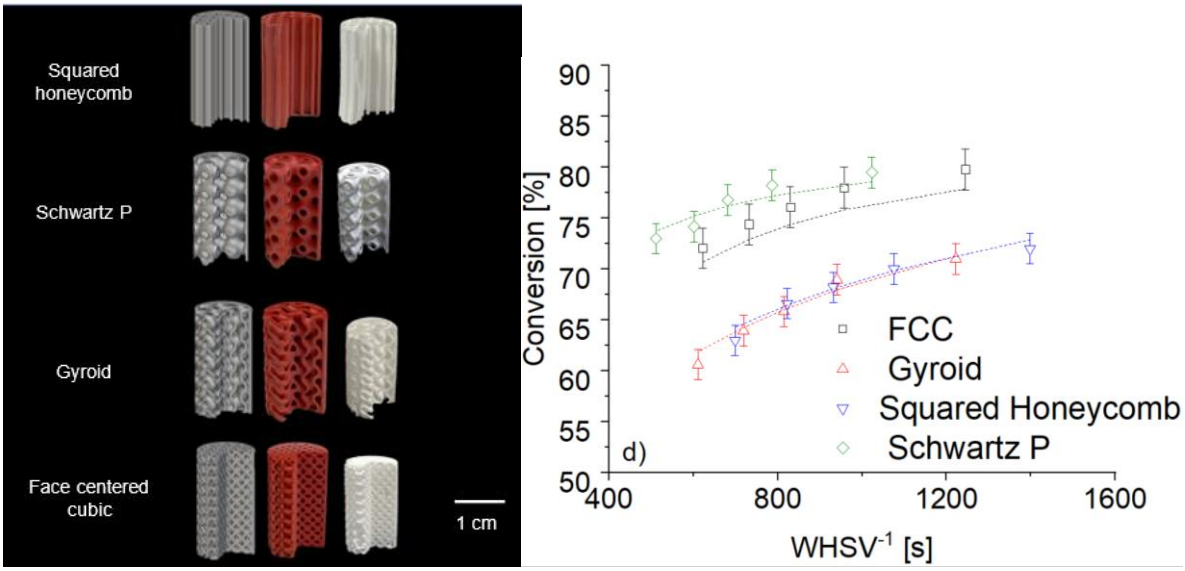
3D printing is expected to revolutionize catalyst shaping as it paves the way for completely new solid catalyst architectures to meet the requirements of high mass and heat transfer rates[1]. Digital Light Processing (DLP) is a very desirable technology among different printing alternatives owing to excellent printing resolution and high printing speed[2]. Herein, a new paradigm to DLP print pure γ-Al_2O_3 catalytic supports is proposed. Infiltration of colloidal nanoparticles of boehmite was adopted to improve the mechanical strength of the catalyst bodies preserving their porosity. The alumina catalysts were loaded in a tubular reactor and their activities were evaluated in continuous ethanol dehydration to diethyl ether. The experiments revealed strong impact of the selected catalyst architecture on the catalyst performance. An advanced 1-D heterogeneous mathematical model employing geometrical features of the catalyst structures was proposed to describe the experimental data. The acquired knowledge was used to 3D print 13X zeolite materials, which have a potential as in situ sorbents in the sorption-enhanced Sabatier reaction to convert CO_2 to methane.

Materials and Methods

The ceramic resin for 3D printing comprised polyethylene glycol diacrylate as the reactive oligomer, phenylphosphineoxide as the photoinitiator, SUDAN III as the UV light adsorber and boehmite as the precursor for γ-Al_2O_3. Propanol was used as non-reactive diluent. The debinded 3D printed objects were immersed in a 5 wt% colloidal boehmite solution to improve the mechanical stability. Four catalyst architectures (squared honeycomb, Schwartz P, face centered cubic and gyroid structures), were designed and printed. The shaped catalysts were loaded in a laboratory-scale tubular reactor operating isothermally at 1 atm and 225-275°C and their activities were evaluated in continuous ethanol dehydration to diethyl ether. The products were analyzed by an online gas chromatograph (GC) equipped a capillary column and thermal conductivity (TC) and flame ionization (FI) detectors. The catalysts were characterized with nitrogen physisorption (specific surface area and pore size distribution) and scanning electron microscopy (SEM). The estimation of kinetic parameters was performed with the aid of the gPROMS 4.0 software, applying the maximum likelihood method.

Results and Discussion

DLP printing enabled to print alumina catalyst bodies with a high precision (Figure 1a). The infiltration of colloidal boehmite successfully improved the mechanical strength of the 3D printed bodies. Indeed, a seven-fold increase in the compressive strength (0.3-2.0 MPa) was observed, making the catalyst structures stable for reaction experiments. The textural properties of the alumina were well preserved: the surface area of the 3D printed catalyst elements was 150 m^2/g, a value only 15% lower than the corresponding alumina in powder form. It was proved that the same method can be used to shape 13X zeolites. Boehmite binder is needed, but the surface areas of the final bodies were high (> 400 m^2/g). The ethanol dehydration experiments revealed significant differences of the catalyst performance at similar space times for the different 3D geometries (Figure 1b). Preliminary parameter estimation effort confirmed that some backmixing takes place within the printed catalyst structures. Therefore, the final mathematical model was based on the axial dispersion concept, including the local variations of the hydraulic diameters within different architectures, which contribute to local variations of the gas velocities as well as mass transfer coefficients. It was observed that, compared to the simplest squared honeycomb monolith, the complex architectures were able to significantly decrease the axial dispersion coefficients, thus improving the local flow segregation. The variations of the axial dispersion coefficients were quantified applying a modified Aris-Taylor correlation in the mathematical model, which provided an accurate description of the experimental data (Figure 1b).



References

1. C. Parra-Cabrera, C. Achille, S. Kuhn, R. Ameloot, *Chem. Soc. Rev*. **2018**, 47, 209-230.
2. L. Sun, P. Dong, Y. Zeng, J. Chen, *Ceram. Int*. **2019**, 45, 23007-23012.

Acknowledgements

This work is part of the activities financed by the Academy of Finland through the Academy Professor grants 319002, 320115, 345053 (Tapio Salmi, Luca Mastroianni). Economic support from Åbo Akademi University Graduate School, Walter Ahlström Foundation and the Finnish Foundation for Technology Promotion (TES) is gratefully acknowledged (Luca Mastroianni).

Hierarchical multiscale analysis of CO_2 electroreduction at high current densities : The onset of transport limitations

Kaustav NIYOGI, Mauro BRACCONI, Matteo MAESTRI*
Politecnico di Milano
Laboratory of Catalysis and Catalytic Processes, Department of Energy
Via La Masa 34, Milano 20156, Italy
**corresponding author: matteo.maestri@polimi.it*

Significance and Relevance

This work provides an explanation of the experimentally observed CO_2 electrolyzer under-performance at high current densities in a gas-diffusion electrode (GDE) based cells using a hierarchical multiscale modeling approach. The low-dimensional model is developed using highly accurate physics-based effective property correlations obtained through high-dimensional simulations and is rigorously validated with experimental CO, H_2 formation rates at different cathodic overpotentials . Our analysis reveals that at high current densities, the diffusional resistances of the GDE strongly influence the experimentally observed reaction rates, thus demonstrating the need to carefully consider such limitations when performing kinetic studies and benchmarking the GDE-based reactor performance.

Preferred and 2nd choice for the topic: Advanced process with electrocatalysis and plasma utilization, Multiscale modeling and advanced simulation aspects
Preferred presentation: Oral / Short Oral

Introduction and Motivations

Low-temperature electrochemical CO_2 reduction offers a lucrative route for re-utilizing the emitted CO_2 towards the production of base chemicals using renewable electricity[1]. However, for commercial adoption, the electrolyzer needs to operate at high current densities using gas diffusion electrodes (GDEs) as an effective medium for transporting the gaseous reactants/ products to the catalyst layer at the interface between the cathode and the electrolyte[2]. At these current densities, the observed reaction rates may deviate from the intrinsic kinetics due to the presence of ohmic and transport resistances originating from the underlying multiphase interfaces in the geometry[3]. This work untangles this complex interplay between charge, mass transport and kinetic processes using a hierarchically refined one-dimensional continuum model for the GDE-assisted CO_2 electroreduction. Our low-dimensional model uses physics-based effective property correlations, derived from high-dimensional simulations of the GDE geometry and ensures a high degree of accuracy in terms of the model predictions. The provided analysis provides potential routes for future reactor design strategies for CO2 electrolyzers towards industrial-scale performance.

Materials and Methods

A one-dimensional multi-region, multiphase reactor-scale model for GDE-assisted CO_2 electroreduction is developed. The model resolves the gas phase diffusion of the reactant, product species, solid phase charge transport through the GDE and couples them with a spatially resolved thin catalyst layer model using flux continuity. The catalyst layer is modeled as a one-dimensional heterogeneous reaction-diffusion system which accounts for the reactant-product dissolution in an aqueous electrolyte and their subsequent participation in homogeneous liquid phase buffer reactions and catalytic charge-transfer reactions. To keep the present analysis tangible, two-electron charge transfer reactions are only considered, i.e. the formation of CO and H_2, using silver catalyst.

Results and Discussion

In the Fig. 1(a), the experimental CO current density (circular, square and triangular markers) are plotted with respect to the cathodic potential *vs. RHE* in the cathodic chamber[4,5]. It can be seen that our model is able to faithfully reproduce the experimental current density data over the range of applied voltages. The current density profile based on intrinsic kinetics without any transfer resistance

is also shown (blue dashed curve) to indicate that as the applied voltage is increased, the experimentally obtained current density profile deviates considerably from the intrinsic kinetics, indicating the possible onset of transport limitations. Our model is able to accurately predict this onset and follow the experimentally observed CO current density. In order to explain this behavior, the model-predicted mean reactant/ product concentrations in the catalyst layer at different cathodic potentials are analyzed. Our analysis shows that as the cathodic potential is increased, the gaseous product build-up in the catalyst layer causes the partial pressure of the reactant to decrease, pushing down the CO_2 saturation concentration at the gas-liquid interface. This in turn, lowers the quantity of CO_2 reaching the electrolyte-submerged catalyst layer and consequently, the reaction rates.

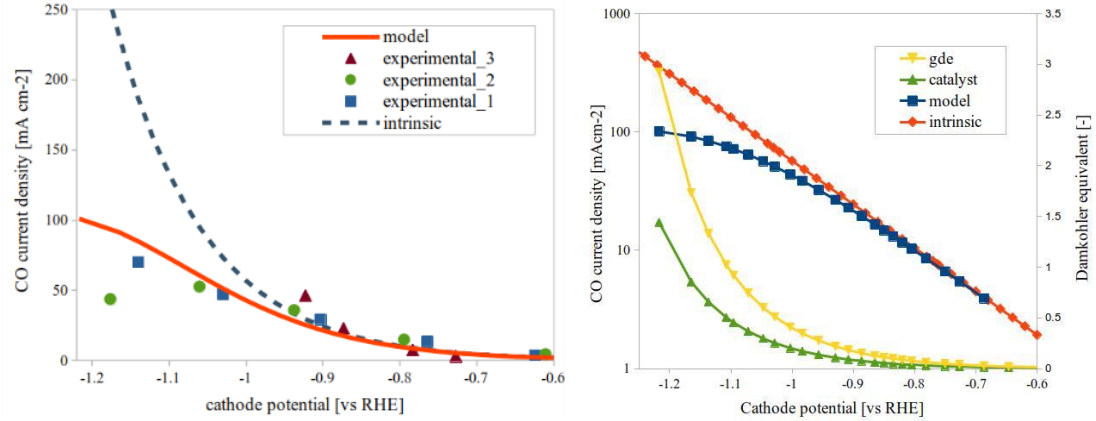


Figure 1. Profiles of (a) average catalyst layer current density, (b) Damkohler equivalents in the GDE, catalyst layer and electrolyte dissolution, overlapped on logarithmic CO current densities, with respect to the cathodic potential *vs. RHE*

To locate the origin of the transport resistance appearing in the cathodic chamber of the electroreduction process (transport in the GDE/ catalyst layer/ bulk reactions), dimensionless quantities characterizing the different transport and kinetic processes are further analyzed. Fig. 1(b) shows the profiles of the Damkohler equivalents for the mass transport through the GDE, the catalyst layer and liquid electrolyte, over-imposed on the CO current density-voltage plot (logarithmic scale). In the entire range of voltage studied, our model suggests that the transport of liquid phase CO_2 from the bulk to catalyst surface offers minimal resistance due to the large surface area and small diffusion path length. However, around -0.85V vs. RHE, where the experimental/ model-predicted current density (blue curve) starts to deviate from the intrinsic kinetics (red curve), the gas phase mass transfer resistances start to play a role, reducing the supply of reactant to the catalytic active sites. In fact, the Damkohler equivalent in the GDE is observed to be higher than the catalyst layer due to its significant thickness in comparison to the catalyst layer. Thus, the developed multiregion continuum model is able to explain the experimentally observed CO_2 electrolyzer under-performance at high current densities and demonstrates the importance of considering the transport resistances in the GDE at high current densities, when measuring reaction rates. Hence, our model provides a useful tool for analyzing and optimizing the reactor design for improved performance at industrially relevant scales.

References

1. Y. Hori, et al., J. Am. Chem. Soc. **1987**, 109, 5022-5023.
2. P.D. Luna, et al., Science, **2019**, 364 eaav3506
3. L. Weng, et al., Energy Environ. Sci., **2020**, 13 3592-3606.
4. S. Verma, et al., Phys. Chem. Chem. Phys., **2016**, 18, 7075–7084.
5. F. P. G. de Arquer, et al., Science, **2020**, 367, 661–666.

Acknowledgements

Financial support from European Union National Recovery and Resilience Plan - NextGenerationEU project ”eCO2toFuel”, MUR sponsored Project: CUP D43C22003090001 (NEST), computational time from the CINECA (Bologna, Italy) are acknowledged.

Modelling the combined HCHO/SCR reaction on $V_2O_5/WO_3/TiO_2$ catalyst in lean gas engine exhaust

Christoph HAHN[1], Sven KURETI[1,*]
Institute of Energy Process Engineering and Chemical Engineering, Chair of Reaction Engineering, TU Freiberg, Fuchsmuehlenweg 9D, 09599 Freiberg, Germany [2]
** sven.kureti@iec.tu-freiberg.de*

Significance and Relevance

The study deals with the kinetic modelling of the combined HCHO and SCR conversion on a $V_2O_5/WO_3/TiO_2$ catalyst in lean gas engine exhaust including the formation and decay of HCN along the catalyst. The modelling of this complex reaction system is novel and is a breakthrough to minimize the secondary emission of HCN formed as a by-product during the reaction of HCHO and NH_3.

Preferred and 2nd choice for the topic: Automotive and stationary emission control / Multiscale modeling and advanced simulation aspects.
Preferred presentation: Oral preferred or Short Oral.

Introduction and Motivations

The emission of greenhouse gases (GHG) is worldwide considered with great concern. Lean-burn gas engines can provide a relevant contribution due to their high efficiency and GHG neutrality when using biomethane. In addition to carbon dioxide (CO_2) and water, gas engine combustion also results in the output of NO_x, carbon monoxide (CO) and hydrocarbons such as HCHO. Due to the strict emission limits a catalytic exhaust gas aftertreatment for NO_x and HCHO is mandatory for stationary lean-burn gas engines. As the SCR with NH_3 is deployed to remove NO_x from the exhaust gas of biomethane fueled lean gas engines the competing consumption of NH_3 by HCHO resulting in the formation of the highly toxic HCN has to be considered. Though the commonly used VWT catalyst is capable to remove both HCHO and HCN from the exhaust gas. Thus, a kinetic model has been developed which describes the conversion of NOx, NH_3 and HCHO as well as the simultaneous formation and decay of HCN.

Materials and Methods

A commercially available cylindrical VWT honeycomb (2.54 cm in diameter and 1 cm in length) with a cell density of 400 cells per square inch (cpsi) and a total V load of 2% is tested in gradient free loop reactor which is suitable to measure the intrinsic chemical kinetics without the influence of mass transfer as confirmed by residence time tests showing a residence time distribution closely to a continuous stirred tank reactor (CSTR). The kinetics of the relevant reactions (see Tab. 1) were tested and determined independently using a flow rate of 600 ml/min (STP) and recycling an inner flow of 50 L/min resulting in a recycle ratio (φ) of 83 except for the NH_3 adsorption and desorption (TPD) and the formation of HCN (plug flow experiments). A kinetic model based on the experimental findings was developed using CSTR balances for the species (Eq. 1) where c denotes the concentration, θ the adsorbed NH_3 species and τ the residence time. The surface balance of the adsorbed NH_3 species is defined by Eq. 2 where Γ represents the surface density which is derived from the NH_3-TPD experiments. The rate equations r_i were described by Arrhenius type expressions (Eq. 3). For the activation energy of the NH_3 desorption a linear dependency on the surface coverage was considered. Furthermore, for the rate approaches of the NH_3 oxidation and the NH_3-SCR the numerical dependencies of the Arrhenius parameters are decoupled using a reference temperature [1] The resulting model was implemented in MATLAB using lsqcurvefit for the parameter estimation and the ode15s function for solving the differential mass balances.

$$\frac{dc_i}{dt} = \frac{c_{in,i} - c_{out,i}}{\tau} + \sum \upsilon_j \cdot r_j \quad (1)$$

$$\frac{d\theta}{dt} = \sum \upsilon_j \cdot r_j \quad (2)$$

$$r_i = A_i \cdot \exp\left(-\frac{E_{A,i}}{R \cdot T}\right) \cdot \prod c_j \cdot \prod \theta \quad (3)$$

Results and Discussion

The suggested overall reaction mechanism and the respective kinetic parameters are presented in Table 1. The model includes the formation of HCN and its subsequent conversion by oxidation as well as hydrolysis. The kinetics of the HCN hydrolysis representing the predominate pathway of the HCN decay is described by a Hougen Watson approach (Eq. 4) [2].

$$r_7 = A_7 \cdot \exp\left(\frac{E_7}{R \cdot T}\right) \cdot c(HCN) \cdot \frac{K(H_2O) \cdot c_0(H_2O)}{(1 + K(H_2O) \cdot c_0(H_2O))^2} \quad (4)$$

Tab. 1. Chemical equations and the respective Arrhenius/model parameter in the kinetic model.

#	Reaction	Arrhenius/model parameter
1	NH_3 (g) + * → NH_3*	A_1 = 4.7e9 s^{-1}; E_1= 0 kJ/mol
2	NH_3* → NH_3 (g) + *	A_2 = 4.9e17 mol/m³/s; E_2 = 114.4 kJ/mol; α_2 = 65.2 kJ/mol
3	NH_3* + NO (g) + 0.25 O_2 (g) → N_2 (g) + 1.5 H_2O (g)	$k_3(T_{ref,3})$ = 16.3 s^{-1}; E_3 = 79.8 kJ/mol; $T_{ref,3}$ = 473.15 K
4	NH_3* + 0.75 O_2 (g) → 0.5 N_2 (g) + 1.5 H_2O (g)	$k_4(T_{ref,4})$ = 33.9 s^{-1}; E_4 = 196.8 kJ/mol; $T_{ref,4}$ = 773.15 K
5	HCN (g) + 1.25 O_2 (g) → 0.5 H_2O (g) + CO_2 (g) + 0.5 N_2 (g)	A_5 = 3.2e5 s^{-1}; E_5 = 69.9 kJ/mol
6	HCHO (g) + 0.5 O_2 (g) → CO (g) + H_2O(g)	A_6 = 2.3e3 s^{-1}; E_6 = 21.9 kJ/mol
7	HCN (g) + H_2O (g) → NH_3* + CO (g)	A_7 = 6.1e10 s^{-1}; E_7 = 93 kJ/mol; K_0 = 1.5e-10 m³/mol; ΔH = -98.8 kJ/mol
8	HCHO (g) + NH_3* + 0.5 O_2 (g) → HCN (g) + 2 H_2O (g)	A_8 = 1.7e10 s^{-1}; E_8= 72.9 kJ/mol

The kinetic model was used to simulate the combined HCHO/SCR reactions in the loop reactor setup with various inlet fractions of NH_3, NO_x and HCHO and provides good prediction of the experimental results, particularly with respect to the HCN and CO formation (Fig. 1). Additionally, the model was transferred to 1D to determine an optimal GHSV of 6700 h^{-1} for a maximal HCN emission of 0.9 ppm.

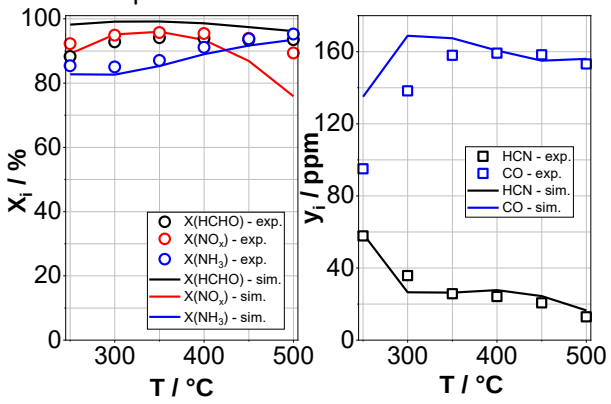


Figure 1. Experimental and simulated data of the combined HCHO/SCR reaction in the loop reactor. Conditions: y_0(HCHO) = 200 ppm; $y_0(NO_x)$ = 500 ppm; $y_0(NH_3)$ = 600 ppm; $y_0(O_2)$ = 5%; $y_0(H_2O)$ = 5%; N_2 balance; F = 0.6 L/min (STP); GHSV = 7000 h^{-1} (STP); φ = 83.

References

1. J. R. Kittrell, *Advances in Chemical Engineering*, 1970, **8**, 97-183.
2. D. Chiche, J.-M. Schweitzer, *Appl. Catal. B: Environ.*, 2017, **205**, 189–200.

Acknowledgements

The authors thank FVV e.V. and AiF for the financial support (IGF Project No. 21977).

Microkinetic modelling of a Pd-based three-way catalyst for stoichiometric natural gas vehicles

Ilyas Yousuf Mir[1], Divesh Bhatia[*,1]
[1]*Indian Institute of Technology Delhi, Department of Chemical Engineering, Hauz Khas, New Delhi 110016, India*
** dbhatia@chemical.iitd.ac.in*

Significance and Relevance

A thermodynamically consistent comprehensive microkinetic model is developed for a Pd-based three-way catalyst for stoichiometric natural gas vehicle exhaust. The model is able to predict the experimental data quite well. A sensitivity analysis is performed to identify the elementary reaction steps which govern the overall rate and the product composition. This work elucidates the detailed microkinetics and rate determining step(s) on the predominantly used Pd-based three-way catalysts, which can be helpful for further catalyst design.

Preferred and 2nd choice for the topic: Automotive and stationary emission control (preferred), Multiscale modeling and advanced simulation aspects (2nd choice)

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivation

Natural gas vehicles are a promising alternative to diesel and gasoline vehicles considering the abundant availability of natural gas reserves and lower NO_x and particulate emissions. Moreover, natural gas, which is mainly composed of methane, produces comparatively lower CO_2 emissions per unit energy produced due to the higher hydrogen to carbon ratio. However, methane being a relatively stable hydrocarbon, the abatement of unburnt methane in the vehicle exhaust poses a demanding challenge, considering the stringent emission norms throughout the world. Pd-based three-way catalysts are predominantly employed for the aftertreatment of natural gas vehicles exhausts under stoichiometric conditions due to the high activity of Pd for methane oxidation.[1]

Various global reaction models have been developed to investigate and predict the catalytic activity of Pd-based three-way catalysts.[2] However, global reaction models use a single rate expression for each overall reaction, which does not contain information on the individual reactions occurring on the surface. Microkinetic modelling, which involves elementary reaction steps, has emerged as a promising tool to gain a deeper insight into the fundamental surface kinetics of the catalyst. Several microkinetic models for CH_4 oxidation under lean conditions and NO reduction under rich conditions on Pd-based catalysts have been developed separately. However, to the best of our knowledge, a comprehensive microkinetic model for a Pd-based three-way catalyst for natural gas vehicles involving CH_4 and NO reduction simultaneously is not available in the literature, which serves as a motivation for this work.

Materials and Methods

The individual methane oxidation and NO reduction mechanisms on Pd (111) surface, obtained from literature, were combined to develop the initial model. A total of 42 elementary steps with 21 surface species and 10 gaseous species were included. A 1D+1D single channel isothermal monolith reactor model was employed to perform the simulations. A sensitivity analysis was conducted to identify the key steps that govern the product composition. The pre-exponential factors of the key steps were obtained by fitting the experimental data from literature [3], with the parameter fitting performed using *'lsqnonlin'* function in MATLAB. During the parameter fitting, thermodynamic consistency of the reaction mechanism was ensured by comparing the standard heat of reaction (ΔH) and standard entropy change (ΔS) of the global reactions (CH_4 oxidation, CO oxidation, and NO reduction to N_2, N_2O and NH_3) obtained from the elementary reaction steps using NIST database.

Results and Discussion

During the preliminary sensitivity analysis, 8 elementary steps were identified as the key steps. A comparison of the model-predicted results and the reported conversion data is shown in Figure 1. The model was able to predict the conversion of CH_4, CO, and NO with reasonable accuracy over the entire lambda range encompassing lean and rich conditions. As shown in Table 1, ΔH and ΔS of all the global reactions were in close agreement with the corresponding values obtained from the NIST database implying that the mechanism is thermodynamically consistent. A sensitivity analysis was performed under lean as well as rich conditions to identify the rate-determining steps. The dissociative adsorption of CH_4 was the key step for CH_4 conversion whereas, the H-assisted dissociation of adsorbed NO played a key role in NO conversion.

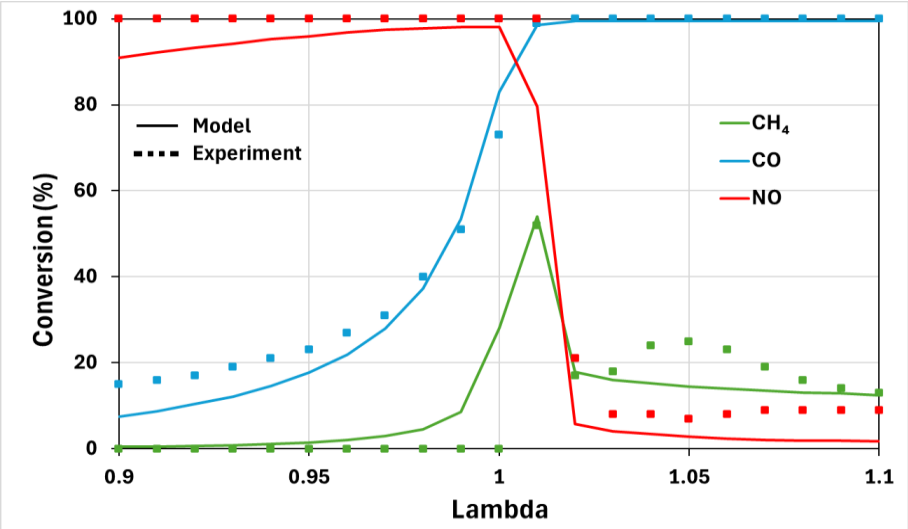


Figure 1. Comparison of model-predicted and experimental product composition at 520 ˚C.

Table 1. Comparison of calculated ΔH and ΔS with NIST database

Reaction	Calculated		NIST database		% error	
	ΔH (kJ/mol)	ΔS (J/mol K)	ΔH (kJ/mol)	ΔS (J/mol K)	ΔH	ΔS
$_4 + 2\ _2 \rightarrow\ _2 + 2\ _2$	-734.3	-5.1	-802.3	-5.1	8.5	0.0
$+ 0.5\ _2 \rightarrow\ _2$	-284.6	-84.0	-283.0	-86.4	0.6	2.8
$NO + 2.5\ _2 \rightarrow\ _3 +\ _2$	-345.4	-165.2	-378.1	-155.8	8.6	6.0
$2\ \ +\ _2 \rightarrow\ _2 +\ _2$	-291.4	-150.1	-340.4	-143.4	14.4	4.7
$2\ \ + 2\ _2 \rightarrow\ _2 + 2\ _2$	-605.9	-115.5	-664.2	-113.6	8.8	1.7

References

1. C. Huang, W. Shan, Z. Lian, Y. Zhang, H. He, Catalysis Science and Technology **2020**, 10, 6407-6419.
2. M. Wang, P. D. Eggenschwiler, D. Ferri, O. Kröcher, Chemical Engineering Journal **2022**, 430, 132848.
3. M. Wang et al., Catalysts **2022**, 12, 373.

Acknowledgements

This work was supported by CSIR (project number 22/0876/23). The authors thank the high performance computing (HPC) facility at IIT Delhi for providing computational resources.

NOx emission control by H_2-SCR over Pt-ZSM5 catalyst in mobile applications

Elisabetta M. CEPOLLARO[1], Stefano CIMINO[1], Michele E. Fortunato[1], Luciana LISI[*,1]
[1]*Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili (STEMS) – CNR, P.le Tecchio 80 – 80125 Napoli, Italy.*
** luciana.lisi@cnr.it*

Significance and Relevance

The development of H_2-fueled vehicles has been proposed to contribute to the limitation of the large fraction of CO_2 emissions associated to the transports sector because hydrogen is a carbon-free fuel. However, there are operating points of the engine promoting the formation of thermal NO_x. The use of H_2, already present on board as a fuel, for the Selective Catalytic Reduction (SCR) of NO_x, replacing ammonia, would avoid the additional device for storage and injection of urea.
ZSM5 supported Pt catalysts have been investigated for SCR of NO_x and the effect of additives considered to inhibit the undesired NO oxidation.

Preferred and 2nd choice for the topic: Automotive and stationary emission control
Preferred presentation: Poster

Introduction and Motivations

In order to mitigate the global warming limiting CO_2 emissions, the development of electric cars has been proposed as primary solution for the transports sector. Nevertheless, approaches still based on Internal Combustion Engine (ICE) have been also considered, such as the use of hydrogen as fuel. Since a completely NO_x free combustion cannot be ensured at all operating points[1] of the H_2-fueled engine which works under lean condition, a catalyzed exhaust after-treatment system is required. H_2 as a reducing agent of NO_x would have the advantage that only one fuel must be carried on board both for propulsion and NO_x reduction, thus avoiding the device for storage and injection of urea, as for the more common NH_3-SCR.
The NO_x reduction by H_2 produces only elemental nitrogen and water:

$$2\ NO + 4\ H_2 + O_2 \rightarrow N_2 + 4\ H_2O \qquad (1)$$

MFI zeolite supported Pt catalysts exhibited higher N_2 selectivity than metal oxide supported catalysts, however, in the presence of excess O_2, Pt can easily catalyse NO oxidation to NO_2[2,3]. In this work, the effect of Pt load at very low levels (0.1-1%) on the activity and selectivity and that of the addition of sodium to depress the oxidation activity of platinum have been investigated.

Materials and Methods

A commercial ZSM5 powder with a SiO_2/Al_2O_3 ratio=23 was impregnated with platinum using an aqueous solution of Tertraammineplatinum(II) chloride hydrate with a platinum/zeolite concentration ratio to obtain 0.1%Pt, 0.5 or 1wt% nominal load. Portions of 0.1%Pt/ZSM5 sample were impregnated with a sodium nitrate solution at different concentration to obtain 5 and 10% Na.
H_2-SCR experiments were carried out in a fixed bed reactor in the temperature range 50-450°C and were also simulated in a DRIFT environmental chamber to investigate the adsorbed NO_x species involved in the reaction.

Results and Discussion

Catalytic tests performed on Pt/Z catalysts with different platinum loads showed that the addition of an amount as low as 0.1%Pt promoted NO conversion to N_2 in the temperature range 80-200°C. The temperature corresponding to the maximum NO conversion decreased with Pt load. Nevertheless,

even with a so low Pt load, at T>200°C NO is mostly oxidized to NO_2. The addition of sodium strongly inhibited the undesired NO_2 formation and, unexpectedly, the N_2O production occurring simultaneously with the main SCR reaction (Fig.1). Catalysts were fully characterized (elemental analysis, XRD, porosimetric analysis, NH_3-TPD) to determine the role of Pt dispersion and of the acid properties on the catalytic performance.

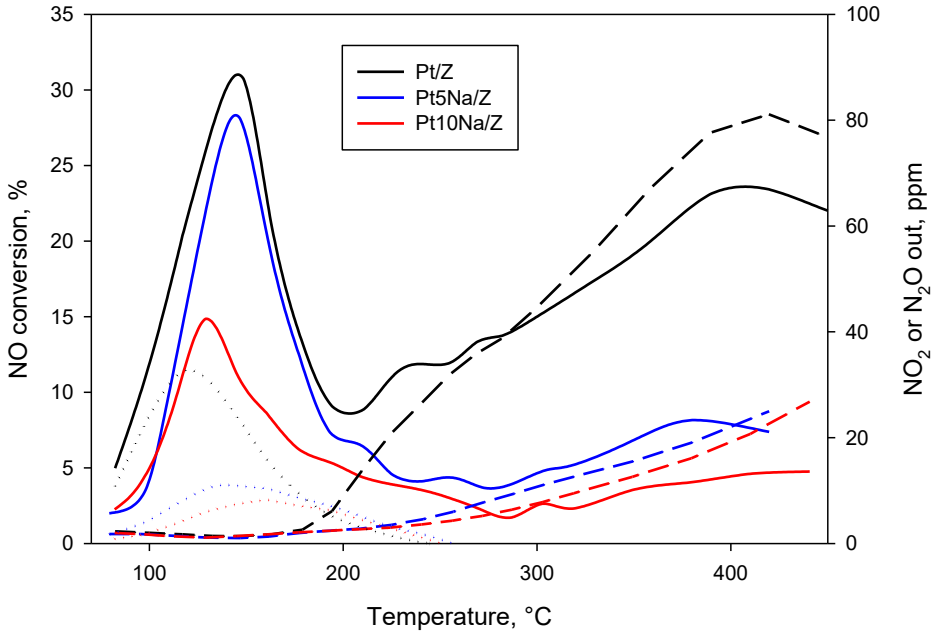


Fig. 1. NO conversion (solid line) and outlet concentration of NO_2 (dashed line) and N_2O (dotted line) of Pt/Z, Pt5Na/Z and Pt10Na/Z.

An Operando-DRIFT study was done to determine the role of adsorbed NOx species involved in the SCR reaction and to identify the possible reaction intermediates.

References

1. D. Koch, A. Sousa, D. Bertram, *SAE Technical Paper* **2019** 2019-01-2178.
2. Y. Guan, Y. Liu, Q. Lv, B. Wang D. Che, *J. Env. Chem. Eng*. 9 **2021** *9* 106770.
3. M. Machida, T. Watanabe, *Appl. Catal. B: Env.* **2004** *52* 281–286.

Acknowledgements

This research was funded by European Union – NextGeneration EU from the Italian Ministry of Environment and Energy Security POR H2 AdP MMES/ENEA with involvement of CNR and RSE, PNRR - Mission 2, Component 2, Investment 3.5 “Ricerca e sviluppo sull’idrogeno”, CUP: B93C22000630006

Pd-ceria catalysts for complete CH_4 oxidation: influence of Pr-doping on sulfur resistance

Enrico SARTORETTI[*,1], Eleonora CALÌ[1], Chiara NOVARA[1], Nunzio RUSSO[1], Debora FINO[1], Samir BENSAID[1]
[1]*Politecnico di Torino, Dept. of Applied Science and Technology, C.so Duca degli Abruzzi 24, Turin, Italy.*
** enrico.sartoretti@polito.it*

Significance and Relevance

Nanostructured Pr-doped Pd-ceria catalysts for complete CH_4 oxidation were studied in the presence of SO_2, in order to investigate how Pr loading affects the behavior of Pd species and influences their regeneration after sulfation. Sulfur can penetrate the bulk of Pr-rich supports, causing structural distortion and defect formation, but the palladium activity is preserved. Sulfation also results in a global reduction of the material and a weakened metal-support interaction. This reduces the beneficial effect of Pr on PdO stabilization at high temperature, but at the same time promotes activity at low temperature, optimizing the PdO/Pd^0 ratio.

Preferred topic: Automotive and stationary emission control
2nd choice topic: Air cleaning and combustion
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Natural gas is regarded as an important energy vector for the energy transition towards a more sustainable society. However, CH_4 emissions must be reduced as much as possible due to its high global warming potential. Catalytic total oxidation is a state-of-the-art method to abate the methane traces in exhaust gases, and Pd-based catalysts are usually employed for activating the CH_4 dissociation.

Since recent research suggested the presence of oxidized Pd^{2+} species to be crucial for catalyzing methane oxidation at high temperature[1], in the last years we synthesized redox Pd supports consisting of pure and Pr-doped ceria[2-4]. We proved that Pr doping enables the conservation of palladium in more oxidized species, thereby reducing the typical loss of activity due to PdO decomposition to Pd, usually observed at 650 – 700 °C during methane oxidation tests[3]. However, the best catalytic activity was achieved with mild Pr-doping (10 at%), since too strong Pd-support interactions is detrimental[2]. An intermediate Pr content also resulted in high activity and stability in the presence of water, thanks to the higher affinity with methane of Pr-doped ceria (observed through in situ FTIR and NMR)[3].

Besides water, sulfur, present in traces in natural gas, is also a known deactivating agent for Pd-based catalysts[5]. Hence, in this work we thoroughly investigated the resistance of Pd/Ce-Pr materials to sulfur poisoning and the role of Pr-doping in this phenomenon.

Materials and Methods

Well-defined nanostructures with different cerium and praseodymium contents were prepared through a hydrothermal synthesis procedure[3] (Ce100 = 100 at% Ce; Ce90Pr10 = 90 at% Ce + 10 at% Pr; Ce50Pr50 = 50 at% Ce + 50 at% Pr; Pr100 = 100 at% Pr). Pd was deposited via incipient wetness impregnation (2 wt%) using a palladium nitrate solution. Catalytic tests of methane oxidation (0.3% CH_4 + 1.2% O_2 in N_2, GHSV = 50 000 h^{-1}), consisting of repeated heating and cooling cycles up to 900 °C (see Figure 1A), were carried out before and after exposure to SO_2 during isothermal reaction (20 ppm, 500 °C, 6 h). The fresh and spent catalysts were comprehensively studied with several techniques, including XRD, N_2 physisorption, Raman spectroscopy, FESEM, TEM, EDX, XPS.

Results and Discussion

Upon exposure to SO_2 during methane oxidation, different behaviors were observed depending on the Pr loading, which seems to influence both the stability and the possibility of the catalyst to be regenerated at high temperature. In particular, Pd/Ce100 exhibited a very rapid drop in activity as soon as SO_2 was sent to the reactor (Figure 1B), whilst Pr doping increased the resistance of the catalyst (only a slight decrease in activity was observed for Ce50Pr50 over 6 h). However, after having exposed the catalyst to higher temperature (900 °C) during a methane oxidation cycle, Pd/Ce100 almost

completely recovered its initial activity (Figure 1C). Instead, the Pr-doped samples exhibited increased activity in the second reaction cycle after sulfation (Figure 1D and 1E), but Pd/Ce50Pr50 dramatically lost the ability to avoid PdO decomposition at high temperature. To understand these phenomena, two spent samples for each catalyst were recovered, one at the end of the fourth reaction cycle (Figure 1A) and the other just after the time-on-stream exposure to SO_2 (TOS).

EDX and XPS analyses of these spent samples revealed the presence of sulfates after TOS, whose content increases with the Pr loading. Moreover, sulfates almost completely disappeared after two reaction cycles in Pd/Ce100, while they were only partially eliminated in the case of Pr-doped catalysts. XRD and Raman measurements indicated a good structural stability for Pd/Ce100 and Pd/Ce90Pr10; conversely, the Pd/Ce50Pr50 catalyst exhibited non-reversible XRD peak splitting and a remarkable increase of the defect-related Raman band after exposure to SO_2. Coupled with TEM-EDX investigations, this information suggests that sulfur can penetrate the bulk of Pr-rich supports, causing structural distortion and defect formation, but without damaging the palladium activity. This also results in a global reduction of the material and a weakened metal-support interaction, as revealed by XPS. The latter effect positively influences activity at low temperature, optimizing the PdO/Pd^0 ratio in Pd/Ce90Pr10, but reduces the beneficial effect of Pr on PdO stabilization at high temperature.

This study explores the behavior of Pr-doped Pd-ceria materials for CH_4 oxidation in the presence of SO_2, providing useful insights for the use of Pr as dopant in real applications.

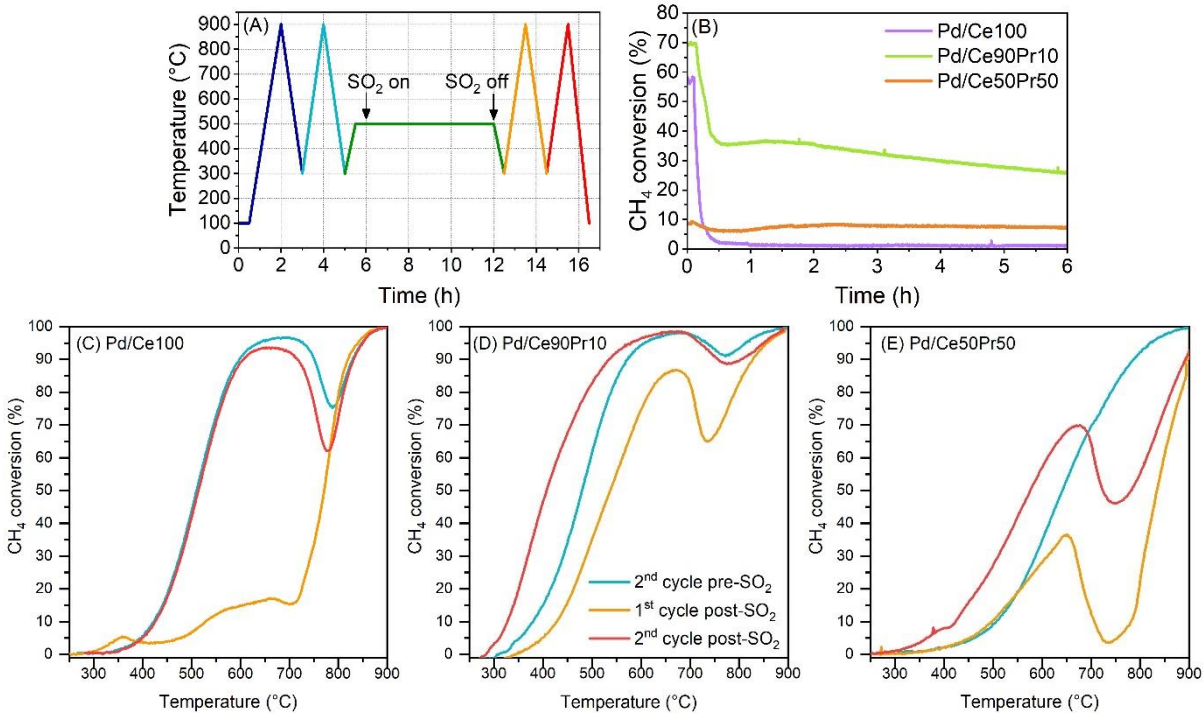


Figure 1 Scheme of the catalytic tests (A). Evolution of CH_4 conversion over time-on-stream (TOS) in the presence of SO_2 (B). Methane oxidation tests (heating runs) performed on the Pd/Ce100 (C), Pd/Ce90Pr10 (C) and Pd/Ce50Pr50 (E) catalysts before and after exposure to SO_2.

References

1. S. Colussi et al., *Chin. J. Catal*. **2020**, *41*, 938–950.
2. S. Ballauri, E. Sartoretti et al., *Catal. Today*. **2022**, *390–391*, 185-197.
3. S. Ballauri, E. Sartoretti et al., *Appl. Catal. B Environ*. **2023**, *320*, 121898.
4. S. Ballauri, E. Sartoretti et al., *ChemCatChem*. **2024**, *16*, e202301359.
5. J. Lin et al., *Appl. Catal. B Environ.* **2024**, *340*, 123283.

Acknowledgements

The REACT-EU program PON Ricerca e Innovazione 2014-2020 (D.M. 1062/2021) and the Italian Ministry of University and Research (MUR) are kindly acknowledged.

Pd speciation and support effect for H_2 SCR

Jieling Shao[1], Zhipeng Wang[2] Phuoc Hoang Ho[1], Yifei Ren[2], Derek Creaser[1], Feng Wang[2] and Louise Olsson[1]
[1]*Chemistry and Chemical Engineering, Competence Centre of Catalysis, Chalmers University of Technology, Gothenburg S041296, Sweden.*
[2] *Department of Chemical Engineering, University College London, London WC1E 7JE, United Kingdom*
** louise.olsson@chalmers.se*

Significance and Relevance

The catalytic performance of SSZ-13 zeolite and BEA zeolite-supported Pd catalysts was investigated. The degree of ion exchange in the two zeolites and the oxidation states under oxidising and reducing conditions were analysed. Complemented by in situ DRIFTS, the results indicated that palladium is more stable within SSZ-13 compared to BEA zeolite. Additionally, BEA zeolite-supported palladium catalysts with a higher degree of ion exchange compared with the SSZ-13-supported one were proved. The reactivity was further assessed under 6 experimental conditions, the results combined with the XAFS measurement revealing that the Pd metallic state is preferred for the NO reduction activity.

Preferred and 2nd choice for the topic: The speciation of Pd on the support of SSZ-13/BEA zeolite for H_2-SCR application.
Preferred presentation: (Oral preferred or short oral)

Introduction and Motivations

Hydrogen has been considered as a great alternative fuel for combustion engines to cope with the greenhouse emission (GHG) requirements. However, NO_x emissions in the exhaust gas are an unavoidable byproduct of the combustion process.[1] Among various approaches, NO_x selective catalytic reduction with hydrogen (H_2-SCR) has been widely proposed. It has been highly reported that H_2-SCR catalysis depends more on the active centres of Pt-group metals.[2] Pd-based catalysts are more promising for H_2-DeNO$_x$ due to their superior selectivity towards producing nitrogen, compared to Pt catalysts.[3] While there are many fundamental studies on Pd-zeolite catalysts, few clearly describe the principles underlying their function in H_2-SCR.[4,5] This study reveals the form of palladium present on the molecular sieve and its dynamic changes during the reaction.

Materials and Methods

SSZ-13 zeolite was synthesized using a hydrothermal method. Pd-based catalysts were prepared using an incipient wetness impregnation (IWI) technique with a loading of 1 wt% supported on SSZ-13 and BEA zeolites. The powder materials were characterized with various techniques such as elemental analysis, CO chemisorption, N_2 physisorption, XPS, and STEM after the hydrothermal pretreatment. NaCl sodium titration was used to determine the amount of ion-exchanged Pd in the catalysts.[6] Catalytic tests were performed with a flow reactor with the monolith sample at 110℃, 200℃, and 300℃ under six sets of reaction conditions including standard H_2-SCR with various H_2 concentrations, NO oxidation, and NO reduction.

Results and Discussion

It has been reported that Pd loading on zeolite exists in a variety of forms, including ionic Pd^{2+} in the zeolite framework (Z_2Pd and ZPdOH) depending upon the Al distribution, PdO_x clusters and smaller Pd particles on the zeolite.[7] With the NaCl titration method, the results indicated that 40% of Pd in Pd/BEA can be exchanged over the calcined IWI synthesized catalyst, while only 4.3% in the Pd/SSZ-13 catalysts which agrees with the results has been reported in the literature.[8] This is due to the larger pore openings of the BEA zeolite compared to SSZ-13. After the hydrothermal pretreatment, the degree of ion exchange increased. Pd oxides and smaller particles on the catalyst surface were further identified by XRD measurements following pretreatment of the samples. Faint characteristic peaks of PdO were observed on the SSZ-13-supported catalysts, due to the fewer Pd ions inside the framework.

In situ DRIFTS measurements of CO and NO adsorption profiles demonstrated that Pd remains more stable in SSZ-13 zeolite compared to BEA zeolite, as indicated by a slower CO-induced reduction and slower transfer of surface intermediate species by NO.

	T / ℃	Gas compostion
S1	200	500ppmNO+10%O_2, 2500 ppm H_2
S2		500ppmNO+10%O_2, 5000 ppm H_2
S3		500ppmNO+10%O_2, 7500 ppm H_2
S4		500ppm NO+10%O_2
S5		500ppm NO+5000ppm H_2
S6		500ppm NO+10%O_2

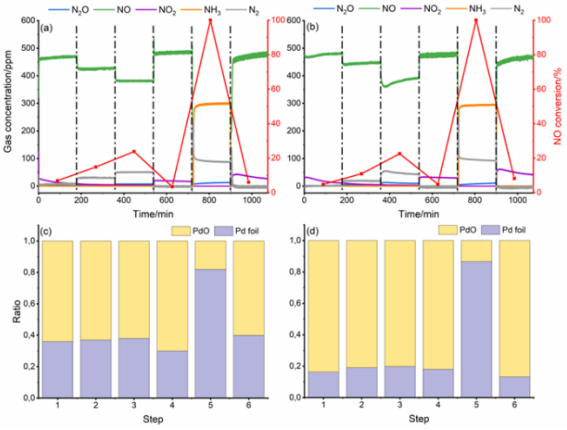


Figure.1 Gas concentrations (N_2O, NO, NO_2, NH_3,N_2) and NO conversion of H_2-SCR at 200 ℃ on (a) Pd/SSZ-13 (b) Pd/BEA catalysts under 6 reaction condition steps (Table, S1-S6) and their LCF results (c-d).

It is shown in Fig.1 that the standard H_2-SCR for the first three steps at 200℃ with increasing H_2 concentration. The NO oxidation reaction in steps 4 and 6 is more reactive on Pd/BEA than Pd/SSZ-13. Step 5 is NO reduction in an anaerobic environment, using a 10-fold excess of hydrogen. The reduction of NO by hydrogen is accompanied by the reduction of Pd to its metallic state. The in-situ dynamic oxidation state change of Pd was measured and verified using the XAFS synchrotron technique. The first three steps have better performances on Pd/SSZ-13 than Pd/BEA, with more Pd metallic states which is proved by LCF analysis in Fig.1c and Fid.1d. There are more Pd oxides on Pd/BEA at Step 4 and Step 6 compared to Pd/SSZ-13, with higher NO oxidation activity. From this, it is clear that the metallic state of palladium favors H_2SCR and the oxidized state is more favorable for NO oxidation reactions. And the BEA-loaded catalyst is more easily oxidized and reduced under the corresponding reaction conditions.

References

1. Z. Hu, R.T. Yang, Ind Eng Chem Res 58, **2019**, 10140–10153.
2. P.G. Savva, C.N. Costa, Catal Rev Sci Eng 53, **2011**, 91–151.
3. P. Granger, F. Dhainaut, S. Pietrzik, P. Malfoy, A.S. Mamede, L. Leclercq, G. Leclercq, Top Catal 39, **2006**, 65–76.
4. Y. Gu, W.S. Epling, Appl Catal A Gen 570, **2019**, 1–14.
5. H.Y. Chen, J.E. Collier, D. Liu, L. Mantarosie, D. Durán-Martín, V. Novák, R.R. Rajaram, D. Thompsett, Catal Letters 146, **2016**, 1706–1711.
6. M. Ogura, M. Hayashi, S. Kage, M. Matsukata, E. Kikuchi, Appl Catal B 23, **1999**, 247-257.
7. K. Mandal, Y. Gu, K.S. Westendorff, S. Li, J.A. Pihl, L.C. Grabow, W.S. Epling, C. Paolucci, ACS Catal 10, **2020**, 12801–12818.
8. Friberg I, Clark A H, Ho P H, et al.Catalysis Today 382, **2021**, 3-12.

Acknowledgements

This study has been funded by the Swedish Energy Agency and carried out in collaboration with Volvo AB, Scania CV, and Johnson Matthey via a strategic vehicle research and innovation (FFI) project (P51458-1). We also appreciate the assistance for Flow-reactor support from Lennart Norberg and Lasse Urholm.

Water Inhibition of NH_3-SCR over Cu-CHA: Measurements and DFT-based kinetic modeling

Shivangi Singh,[a,b] Yingxin Feng[a], Ton V. W. Janssens[b], and Henrik Grönbeck[a]
[a]Department of Physics and Competence Centre for Catalysis, Chalmers University of Technology, SE-412 96 Göteborg, Sweden
[b]Umicore Denmark ApS, DK-2970 Hørsholm, Denmark

Significance and Relevance

Understanding the interaction between water and zeolite catalysts is vital not only for diesel exhaust treatment but also extends to exhaust systems for hydrogen combustion in internal combustion engines (ICEs), where water vapor is present in large amounts. Water is measured to significantly impact ammonia-selective catalytic reduction (NH_3-SCR) over Cu-CHA. Atomic-level understanding is provided by a DFT-based kinetic model.

Preferred and 2nd choice for the topic:
Automotive and stationary emissions control
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Cu-exchanged chabazite (Cu-CHA) is a widely applied catalyst for selective catalytic reduction of nitrogen oxides in oxygen excess.[1] However, the potential application of Cu-CHA in hydrogen-fueled internal combustion engines (H_2-ICEs) presents new challenges due to the high partial pressures of water vapor produced during hydrogen combustion.[2]

Herein, we present flow reactor measurements to study the NH_3-SCR rate over Cu-CHA with H_2O partial pressures in the range from 2% to 25%. The measurements are corroborated with Density Functional Theory (DFT) calculations and DFT-based microkinetic modeling to understand the atomic-level mechanisms for the H_2O inhibition of the NH_3-SCR reaction.

Materials and Methods

A Cu-CHA catalyst (Si/Al = 6.7, 3.2 wt% Cu) was prepared via Cu-nitrate impregnation and calcination (600 °C, 2 h). For SCR measurements, 4 mg catalyst (150–300 µm) mixed with 76 mg SiC was degreened (10% O_2, 500 °C, 30 min) and exposed to 500 ppm NO, 600 ppm NH_3, 10% O_2, and 2–25% H_2O in N_2 at 200 °C, at the flow rate of 18 NL/h.
Density functional theory (DFT) calculations were performed using the Vienna Ab- Initio Simulation Package (VASP). Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional with Hubbard- U and van der Waals corrections was applied using a plane wave basis with the kinetic energy cutoff at 480 eV. The chabazite structure is described with a periodic rhombohedral unit cell, which contains 12 tetrahedral Si-sites. We use the experimentally determined lattice parameters which are fixed during the structural optimizations.

Results and Discussion

The effect of water on the NO_x conversion is studied under dry and wet conditions (5% water). We find that water reduced the conversion in the temperature range of 160°C to 260°C. Measuring the NO_x conversion for pressures in the range from 0% to 25% at 200°C supports this trend, with a reduction in NO_x conversion for water pressures higher than 2%. The NO_x conversion is used to calculate the reaction order with respect to water, we find a change in the reaction order in water from -0.16 at 2% water to -1.11 at 25% water. The measured reaction order for water follows the simple equation: $-3.23 \cdot \exp(0.76 \cdot \ln(p(H_2O)))$ as shown figure 1 (A).

Density functional theory (DFT) calculations are performed to explore the mechanism for water inhibition. The calculations investigate water adsorption on key intermediates in a previously

suggested reaction cycle [3,4]. O_2 is at low temperatures activated by adsorption on a pair of NH_3-solvated Cu+ species $[Cu^+(NH_3)_2]$ forming a Cu-peroxo species, $[Cu_2(NH_3)_4O_2]_2^+$. NH_3 and NO couple twice over the Cu-peroxo species, resulting in the formation of two H_2NNO and a $[Cu_2(NH_3)_4OHOH]^{2+}$ complex. Previous simulations indicate that $[Cu_2(NH_3)_4O_2]_2^+$ and $[Cu_2(NH_3)_4OHOH]^{2+}$ together with $[Cu_2(NH_3)_5O_2]_2^+$ are the most abundant intermediates at temperatures around 200°C [3,4]. The present DFT calculations show that H_2O adsorption competes with NO adsorption on the Cu-sites on $[Cu_2(NH_3)_4O_2]_2^+$ and $[Cu_2(NH_3)_4OHOH]^{2+}$.

By accounting for H_2O adsorption in the DFT-based microkinetic model [4], we are able to reproduce the experimentally measured reaction orders, which supports the inhibitory effect of H_2O. The simulated TOF aligns well with experimental data when slight adjustments have been done to the H_2O entropy of adsorption as well as a weak partial pressure-dependent term in the H_2O Gibbs free energy of adsorption is introduced as shown in Figure 1(B).

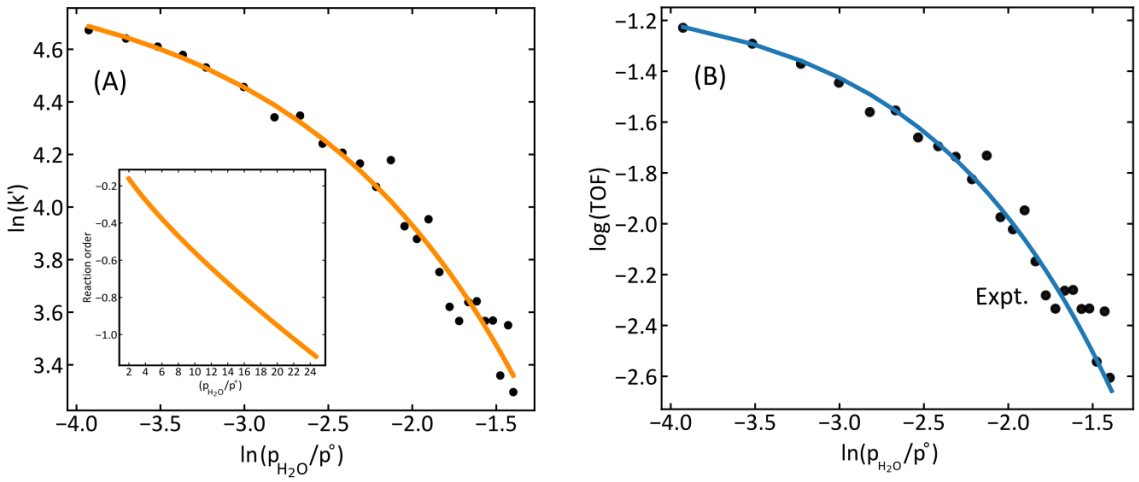


Figure 1: (A) Natural logarithm of the rate constant ln(k') as a function of the natural logarithm of partial pressures of water and (B) Logarithm of simulated TOF as a function of logarithm of the partial pressures of water.

References

[1] A.M. Beale et al., *Chem. Soc. Rev.*, **2015**, *44*, 7371-7405.
[2] C.M. White et al., *Int. J. Hydrogen Energy*, **2006**, *31*, 1292-1305.
[3] L. Chen et al., *ACS Catal.*, **2020**, *10*, 5646-5656.
[4] Y. Feng et al., *ACS Catal.*, **2021**, *11*, 14395-14407.

Acknowledgements

We acknowledge support from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement no. 955839 (CHASS). The calculations have been performed at PDC (Stockholm) and NSC (Linköping) through a NAISS grant (2022/3-14). The Competence Centre for Catalysis (KCK) is hosted by Chalmers University of Technology and financially supported by the Swedish Energy Agency (52689-1) and the member companies Johnson Matthey, Perstorp, Powercell, Preem, Scania CV, Umicore and Volvo Group.

Catalytic co-pyrolysis of lignocellulose and non-edible vegetable oil using n-ZSM-5: synergistic effects for aromatic hydrocarbons production

Maurizio PAGANO[1, 2], Jennifer CUETO[1], Inés MORENO[1, 2], David P. SERRANO[*, 1, 2]
[1] *Thermochemical Processes Unit, IMDEA Energy, 28935 Móstoles, Spain.*
[2] *Chemical and Environmental Engineering Group, Rey Juan Carlos University, 28933 Móstoles, Madrid*
** david.serrano@imdea.org*

Introduction and Motivations

The catalytic co-pyrolysis of lignocellulose with other H-rich feedstocks is gaining interest as a promising process for the production of biofuels and chemicals, since it may overcome some of the main drawbacks of lignocellulose pyrolysis, such as low yields of aromatic hydrocarbons (AR), fast catalyst deactivation and high bio-oil oxygen content[1]. An acid catalyst is needed to produce a higher quality bio-oil by promoting cracking, deoxygenation, and aromatization of the pyrolysis vapors. In this context, zeolites are the most promising materials to produce AR due to their acidic and textural properties[2]. Plastic residues, waste tires and methane have been investigated for the co-processing with lignocellulose, and synergistic effects have been observed in terms of yield of fuel-grade hydrocarbons[1]. Although the catalytic pyrolysis of lipids is a known and well-studied process to produce AR[3], the literature about the catalytic co-pyrolysis of lignocellulose and vegetable oils employing zeolites as catalyst is very scarce. In this work, a continuous bench-scale reaction system was used to evaluate the synergistic effects arising from the co-processing of these types of feedstocks in terms of AR production and catalyst stability along the time on stream, and to optimize the system by studying different feed ratios and pyrolysis temperatures.

Materials and Methods

Oak tree (Ence, Spain) and Camelina oil (Camelina Company, Spain) were used as feedstocks for the catalytic co-pyrolysis experiments. They were continuously fed into an ex-situ downdraft fixed-bed reactor divided in two sections: pyrolysis and catalytic zones, which were heated independently. Different Oak/Camelina oil (Oak/Cam) mass ratios were studied (1.5, 2.3, 4, and 9), with a total feeding rate of 5 g/h. Two pyrolysis temperatures were studied for the pyrolysis zone of the reactor (350 and 500 °C), while the catalytic one was kept at 450 °C in all cases. A commercial nano crystalline ZSM-5 zeolite (n-ZSM-5) was used as catalyst (see main properties in Table 1), with a fixed loading of 3 g. The total duration of the runs was 4 h, with bio-oil and gas sampling every hour to monitor their yield and composition over time.

Table 1. Physico-chemical properties of the n-ZSM-5 catalyst.

Sample	Si/Al[a] mol	S_{BET}[b] $m^2.g^{-1}$	S_{MICRO}[b] $m^2.g^{-1}$	V_{TOT}[b] cc/g	V_{MICRO}[b] cc/g	$C_{BRONSTED}$[c] mmol/g	C_{LEWIS}[c] mmol/g
n-ZSM-5	50	366	274	0.458	0.171	0.252	0.034

[a] from ICP; [b] from Ar-isotherm at 87 K; [c] FT-IR/pyridine adsorption-desorption (150 °C).

Results and Discussion

As shown in Figure 1.A, the overall bio-oil yield (mean of 4 h of reaction) increases with the amount of camelina oil introduced in the feedstock. In all cases, this bio-oil is rich in AR compounds (mainly in xylene, toluene, benzene, and naphthalene) due to the aromatization activity and shape selectivity provided by the n-ZSM-5 catalyst. However, the pyrolysis of lignocellulose also produces heavy phenolic compounds and other oxygenated hydrocarbons which reduce the bio-oil quality and catalyst stability. Thus, the co-processing of oak with camelina oil leads to a 60% of reduction in the bio-oil oxygen content (Figure 1.A) and a 20% of improvement in the carbon yield of aromatic hydrocarbons referred to both feedstocks (AR-C_F yield) (Figure 1.B) compared to the additive results calculated as the weighted yields obtained from the pyrolysis of the individual feedstocks (indicated as “Calc.”). These results indicate the occurrence of a significant synergistic effect due to the ability of the vegetable oil

vapors to act as H donor, thus promoting the deoxygenation of lignocellulose molecules. On the other hand, the increased concentration of olefins from the cracking of the vegetable oil enhances the extension of Diels-Alder condensation reactions with furans[4] produced from lignocellulose, resulting in a highly deoxygenated liquid product with an AR concentration higher than 90 wt%. However, the intensity of the synergistic effect is minimally affected by the feeding ratio, suggesting the presence of a limiting factor such as the availability of reactants, especially furans, or the saturation of the catalyst active sites. However, this result could be a positive feature as it would offer flexibility in terms of process design based on feedstocks availability, prices, and target production volume.

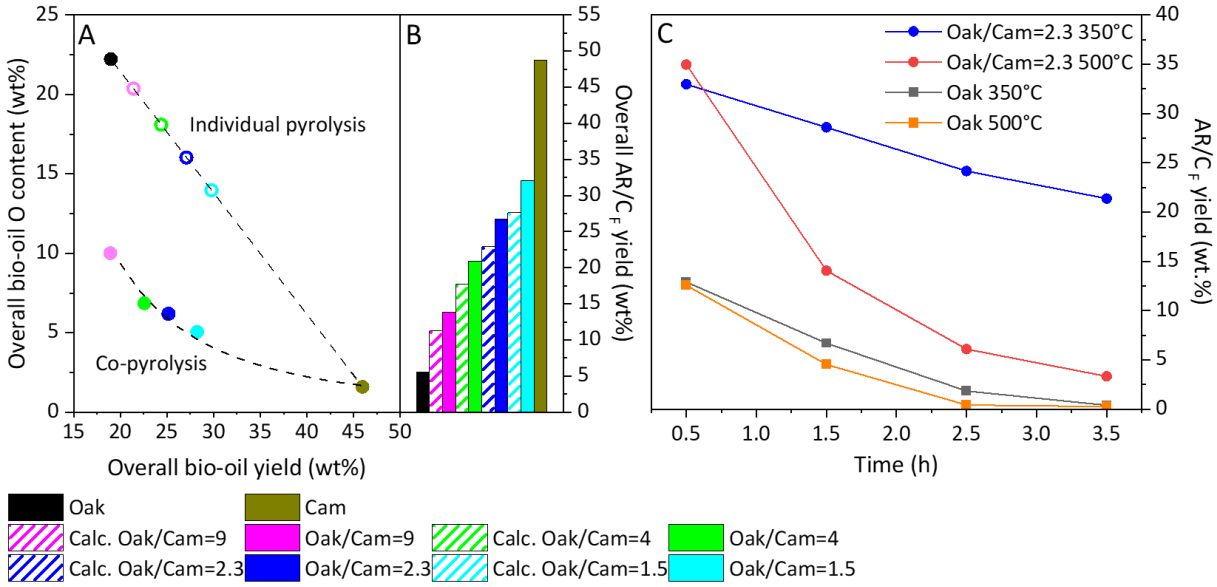


Figure 1. (A) Overall bio-oil mass yield vs O content at different Oak/Cam ratios. (B) Overall AR-C_F yields at different Oak/Cam ratios. (C) AR/C_F yield vs time on stream for oak pyrolysis and co-pyrolysis at different reactor pyrolysis zone temperatures.

On the other hand, the temperature of the pyrolysis zone of the reactor strongly influences the extent of the synergistic effect. Thus, the catalyst stability is sharply improved when working at a relatively low temperature (350 °C) under co-pyrolysis conditions, as shown in Figure 1.C, while only a slight difference between the two temperatures can be observed when processing oak biomass alone. A higher temperature favors the release of lignin oligomers and other oxygenated derivatives, which are known to be major coke precursors. These species competitively occupy the zeolite acid sites and promote secondary reactions that reduce both the selectivity to AR and the zeolite lifetime by blocking its pores[5]. Thus, the zeolite benefits derived from the synergy are strongly enhanced when combined with a low temperature pyrolysis of the lignocellulose.

References

1. S. Zhong, B. Zhang, C. Liu et al., J Anal Appl Pyrolysis **2022**, 164, 105544
2. H. Hernando, A. Hernández-Giménez, C. Ochoa-Hernández et al., Green Chem. **2018**, 20(15)
3. X. Wang, Y. Whang, X. Jin et al. Appl. Catal. A **2022**, 643, 118769
4. M. Ahmed, N. Batalha, H. Mahmudul et al., Bioresour. Technol. **2020**, 310, 123457
5. B. Luna-Murillo, M. Pala, A.L. Paioni et al., ACS Sustain. Chem. Eng. **2021**, 9, 291-304

Acknowledgements

The present work was financed by the Spanish Ministry of Science and Innovation (ADBIOCAP, PID2020-114740RB-C21).

Exploring the technical and environmental potentialities of rice husk-derived biochar for H_2S removal

Francesca Demichelis[1*], Premchand Premchand[1], Camilla Galletti[1], Fabio Alessandro Deorsola[1], Raffaele Pirone[1], Debora Fino[1], Guido Saracco[1]

[1]Politecnico di Torino, Department of Applied Science and Technology (DISAT), Corso Duca degli Abruzzi 24, 10129 Torino, Italy

** francesca.demichelis@polito.it*

Significance and Relevance

Rice Husk (RH) and biochar were treated with KOH and NaOH before and after pyrolysis at 600 °C under N_2 and CO_2 atmospheres. Alkali pre-activation in CO_2 reduced biochar yield and carbon content but significantly improved specific surface area (SSA) and pore volume (PV), with KOH being more effective than NaOH. The highest SSA and PV (178.4 m^2/g and 0.60 cm^3/g) were achieved with pre-activated KOH-RH in CO_2 (KOH_RH_CO2). H_2S removal tests showed commercial activated carbon (CAC) and KOH_RH_CO2 performed best. At H2S = 35 ppm at GHSV = 3822 h^{-1}, CAC and KOH_RH_CO2 achieved 65.12 and 40.52 mg H_2S/g, with carbon footprints of 0.12 and 0.08 gCO_2eq/g H_2S removed, respectively.

Preferred and 2nd choice for the topic: 1°. Green chemistry and biomass transformation, renewable resources conversion. 2nd Circular economy.
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The Next Generation Level Europe program promotes the green transition by considering renewable energy and waste management. Biogas, produced via anaerobic digestion, is a key renewable energy source but contains toxic H_2S, which must not exceed 5 ppm (WHO). Traditional methods use activated carbon[1], but an alternative can be the biochar produced through slow pyrolysis (sPY) of agricultural waste like rice husk (RH) (European RH production is around 560000 t/y). This study assessed the production and environmental feasibilities of replacing commercial activated carbon with RH-derived biochar as well as activated to remove H_2S by reducing fossil resource consumption, promoting biomethane production, and converting agro-waste into valuable materials.

Materials and Methods

Figure 1 depicts the adopted approach. Pre- and post-activation treatments aimed to enhance biochar's physical and chemical properties. RH was impregnated with KOH or NaOH in a ratio equal to 1:1, before and after pyrolysis at 600°C at 15 °C/min, for 1 h under N_2 or CO_2 atmospheres. The sPY was performed in a fixed-bed reactor and the conditions were based on our previous study[2]. The most promising biochars and commercial activated carbon (CAC) (as a reference), were tested as adsorbents in H_2S dynamic removal tests. These tests were conducted in a vertical fixed-bed reactor at continuous flow, atmospheric pressure, at 25 ± 2 °C, by varying H_2S from 35 to 700 ppm and gas hourly space velocity (GHSV) between 30573 and 3822 h^{-1}. The RH, biochars, and spent biochars were chemically and physically characterized. The biochars with the highest H_2S removal were compared through an ex-ante carbon footprint analysis (CF) (ISO 14067) to identify the best compromise between technical and environmental performances.

Results and Discussion

RH and biochar were activated with KOH and NaOH before and after pyrolysis at 600 °C under N_2 and CO_2 atmospheres. Results indicated that pre-activation with alkalis under CO_2 slightly decreased biochar yield and carbon content, compared to N_2. Alkali pre-activation in CO_2 significantly increased the specific surface area (SSA) and pore volume (PV) of biochars, with KOH more effective than NaOH (Figure 2). Pre- and post-activation with KOH were better than with NaOH, hence H_2S experiments tested: pre-and post-activated biochar with KOH under CO_2, RH-biochar produced under CO_2 and N_2

as a positive control, and commercial activated carbon (CAC) as reference. The performances of these materials were tested at H_2S concentrations of 35 and 70 ppm at three GHSVs: 30573, 15286, and 7643 h^{-1}. Increasing the concentration from 35 to 70 ppm all materials' adsorption capacity and breakthrough time decreased. Additionally, higher GHSV reduced adsorption capacity and breakthrough time. The best performances were observed with CAC and biochar from RH pre-treated with KOH (KOH_RH_CO_2). Hence, these two materials were deeply investigated increasing H_2S concentration from 35 to 700 ppm and decreasing the GHSVs from 7643 to 3822 h^{-1} (Figure2). Higher H_2S concentrations reduced the adsorption capacity for both materials due to faster breakthrough times, caused by a greater concentration gradient and increased mass transfer coefficient. However, lower GHSVs improved adsorption capacity and breakthrough times[3]. The best results were obtained at H_2S = 35 ppm at GHSV = 3822 h^{-1}: CAC and KOH_RH_CO_2 achieved 65.12 and 40.52 mgH_2S/g, respectively. Under these conditions, the CF values for CAC and KOH_RH_CO_2 were 0.08 and 0.12 g CO_2 eq/g H_2S removed, respectively.

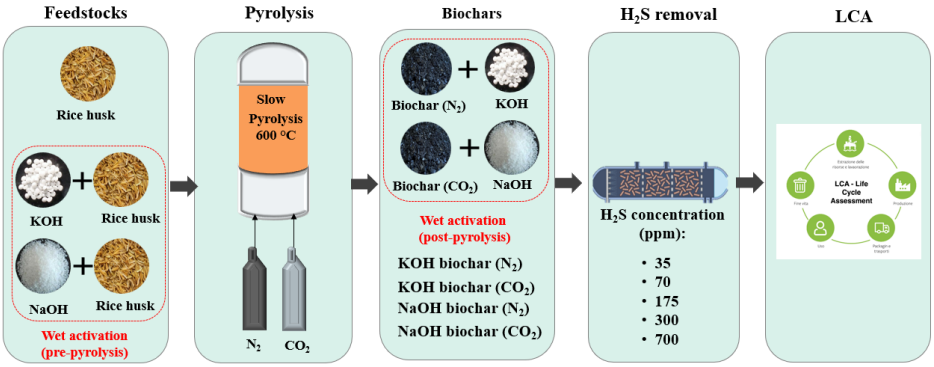


Figure 1: adopted approach to prepare the biochars and test them

	Specific surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})
Without treatment		
Untreated BC (N_2)	55.7	0.018
Untreated BC (CO_2)	141.0	0.084
Pre-pyrolysis activated		
NaOH-BC (N_2)	102.3	0.268
NaOH-BC (CO_2)	123.0	0.255
KOH-BC (N_2)	117.6	0.341
KOH-BC (CO_2)	178.4	0.598
Post-pyrolysis activated		
BC (N_2)-NaOH	68.7	0.127
BC (CO_2)-NaOH	107.6	0.101
BC (N_2)-KOH	99.0	0.197
BC (CO_2)-KOH	152.0	0.311

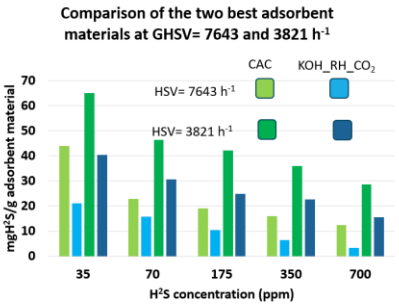


Figure 2: Characterization of adsorbent materials and results of H_2S removal test on the most promising adsorbent materials (commercial activated carbon (CAC) and pre-activated RH with KOH).

References:

1. Javier, Ó., Bermúdez, F., Giraldo, L., Sierra, R., Juan, R., Moreno, C., 2023. Removal of hydrogen sulfide from biogas by adsorption and photocatalysis : a review. Environ. Chem. Lett. 21, 1059–1073. https://doi.org/10.1007/s10311-022-01549-z
2. Premchand, P., Demichelis, F., Chiaramonti, D., Bensaid, S., Fino, D., 2023. Journal of Environmental Chemical Engineering Biochar production from slow pyrolysis of biomass under CO_2 atmosphere : A review on the effect of CO 2 medium on biochar production, characterization, and environmental applications. J. Environ. Chem. Eng. 11, 110009. https://doi.org/10.1016/j.jece.2023.110009
3. Cui, S., Zhao, Y., Liu, Y., Huang, R., Pan, J., 2021. Preparation of Straw Porous Biochars by Microwave-Assisted KOH Activation for Removal of Gaseous H 2 S. https://doi.org/10.1021/acs.energyfuels.1c02241

Green syntheses of Ni-Mo-Al catalysts for deoxygenation of vegetable oil into green diesel: green metrics of syntheses and deoxygenation performances

Andrea DI GIULIANO *[,1], Paola PIETRANGELI [1], Stefania LUCANTONIO [1], Giuseppe DI VITO NOLFI [2], Katia GALLUCCI [1], & Leucio ROSSI [2]

[1] *University of L'Aquila, Department of Industrial and Information Engineering and Economics, Piazzale E. Pontieri 1, L'Aquila, Italy.*

[2] *University of L'Aquila, Department of Physical and Chemical Sciences., Via Vetoio, L'Aquila, Italy.*

** andrea.digiuliano@univaq.it*

Significance and Relevance

To make a catalytic process sustainable in its overall life cycle, the synthesis of the needed catalyst should be as sustainable as possible too. This idea was applied to two new syntheses of Ni-Mo-Al catalysts for the deoxygenation (DO) of vegetable oils into green diesel, a process of industrial relevance in the energetic transition. Both methods aimed to fulfil some principles of Green Chemistry and Green Engineering: in one case, by avoiding the use of any solvent; in the other, by tending to implement a "one-pot" method. Sustainability performances of catalyst syntheses were evaluated by some green metrics such as: Effectiveness Ratio (R_{eff}); Reaction Mass Efficiency (RME); Mass Productivity (MP); Energy Intensity (EI). DO catalytic tests were performed too.

Preferred and 2nd choice for the topic:
Green chemistry and biomass transformation, renewable resources conversion
Sustainable and clean energy production and transport (2nd choice)

Preferred presentation: Oral preferred

Introduction and Motivations

The ACS' twelve Principles of Green Chemistry [1] and twelve Principles of Green Engineering [2], among several recommendations, suggest limiting the usage of solvents or the number of steps in chemical syntheses to improve the sustainability of related products. This approach can be applied to the synthesis of catalysts too: the improvement in the sustainability of the catalyst synthesis might be beneficial to the overall sustainability of the process in which the catalyst is involved.

The heterogeneous catalytic deoxygenation (DO) of fatty biomasses (e.g., vegetable oils) was taken as a case of study to evaluate this approach. DO converts fatty biomasses and H_2 into alkanes known as green diesel (carbon atoms in the alkane molecule from 15 to 18) [3].

A formulation of the DO catalyst in terms of ratios between NiO, MoO_3, Al_2O_3 was established, and two new synthesis methods were developed:

(i) a Solventless synthesis (OM, "Oxides Mixed") involved calcinations of Ni, Mo, and Al precursor salts and the mechanical mixing of resulting oxides. (e.g., fulfilling with principle 5 of Green Chemistry "solvents and auxiliaries"); it is under patenting procedure [4];

(ii) a One-pot synthesis (OMA = "Oxides Mixed in Aqueous medium") involved the wet-mixing of Ni, Mo, and Al precursor salts in an aqueous medium, and one overall calcination. (e.g., fulfilling with principle 4 of Green Engineering "maximize efficiency").

The sustainability performances of these two synthesis methods were compared by estimating green metrics. The solid catalysts were characterized. The DO catalytic performances were evaluated for the two OM and OMA catalysts.

Results and Discussion

The XRD (X-Ray Diffraction) characterization of the two catalysts OM and OMA (not shown) evidenced the formation of different crystalline phases: OM contained Ni, Mo and Al not combined one to the other; OMA contained some crystalline phases combining Ni-Mo and Al-Mo.

The sustainability of the two syntheses of OM and OMA was evaluated by four green metrics:

(i) Effectiveness Ratio: $=$ ———————

(ii) Reaction Mass Efficiency: $=$ ———————

(iii) Mass Productivity: $=$ ———————————————— $+$,

(iv) Energy Intensity: $=$ ———————————— h h

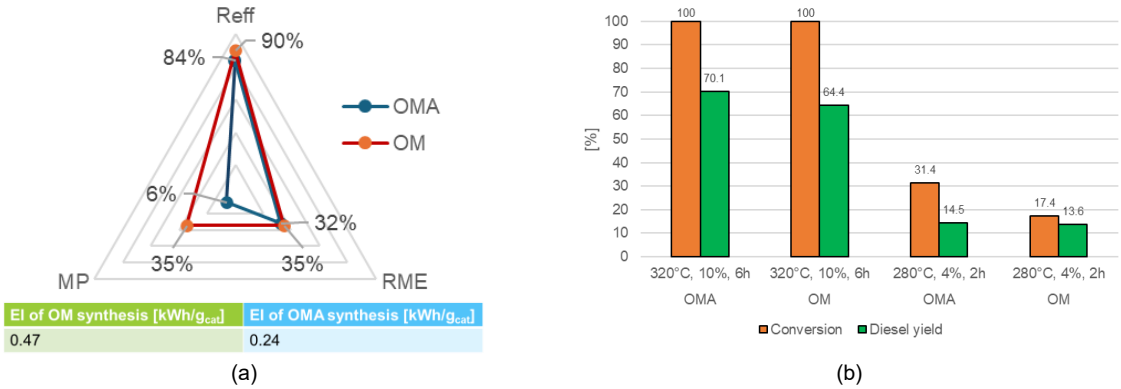
Figure 1(a) shows the comparison of the green metrics: as to "mass" green metrics (, ,), only MP was significantly different, i.e., lower in the case of OMA synthesis because of the use of a solvent; on the other hand, OMA synthesis appeared more energetically advantageous, because of the use of only one calcination in the place of the three calcinations of OM.

The DO performances of OM and OMA were evaluated by catalytic tests on commercial rapeseed oil (2 g) in a batch laboratory-scale reactor, at two sets of conditions: {320°C-10% (catalyst/oil mass ratio)-6 h of reaction} or {280°C-4% (catalyst/oil mass ratio)-2 h of reaction}. The DO liquid product was characterized by gas-chromatographic techniques [5], to estimate:

(i) DO conversion: $= (1 -$ ———————)

(ii) DO diesel yield: $=$ ———————————— h 15,16,17,18

Figure 1(b) compares catalytic performances of OM and OMA: both catalysts carried out DO satisfyingly at {320°C-10% (catalyst/oil mass ratio)-6 h of reaction}, according to and in the literature [3]; at the other set of conditions {280°C-4% (catalyst/oil mass ratio)-2 h of reaction}, the OMA catalyst showed a higher catalytic activity (higher) and a lower selectivity towards alkanes (similar) than those expressed by OM.



(a) (b)

Figure 1 Comparison between OM and OMA catalysts: (a) Radar Plot to compare mass Green Metrics and values of EI; (b) DO performances

Overall, two new green-syntheses were proposed to produce Ni-Mo-Al catalysts that worked for the DO of rapeseed oil into green diesel. Some sustainability aspects of these syntheses were evaluated: the mass green metrics favour OM, whereas energy intensity favour OMA; on the other hand, the additional mass involved in OM synthesis is water (the best choice among solvents in terms of sustainability).

References

1. https://www.acs.org/greenchemistry/principles/12-principles-of-green-chemistry.html
2. https://www.acs.org/greenchemistry/principles/12-design-principles-of-green-engineering.html
3. S. Lucantonio, et al. *Energies* **2023** *16.2*, 844.
4. "CATALIZZATORE SOLIDO DI IDROTRATTAMENTO, RELATIVA SINTESI E SUO UTILIZZO IN PROCESSO DI DEOSSIGENAZIONE DI TRIGLICERIDI "Domanda numero: 102023000023556.
5. AOAC, Official Methods of the AOAC International, **2000** 24-26.

Acknowledgements

The authors thank Prof. Claire Courson and Prof. Valeria Daniele for XRD characterizations

Assessment of low PGM catalyst for Ammonia cracking

Giovanni CARDOLINI RIZZO *, Carlo CASTELLI, Alessandro MONTEVERDE.
Politecnico di Torino,Department of Applied Science and technology (DISAT),Torino,Italy.
**giovanni.cardolini@polito.it*

Significance and Relevance

This study highlights the potential of advanced screening techniques to identify cost-effective alternatives to high-cost catalysts for low-temperature ammonia decomposition. By incorporating yttrium (Y) and zirconium (Zr), the ruthenium (Ru) content was successfully halved while maintaining high catalytic activity with minimal performance loss. Detailed investigations revealed that substituting Ru with Y or Zr did not impact the apparent activation energy of the catalysts, demonstrating their viability as economical and efficient options for ammonia cracking applications.

Preferred and 2nd choice for the topic: H2 storage and transportation, green H2 production, hydrogen vectors; Catalysis to electrify the chemical production
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster): Oral/Short Oral

Introduction and Motivations

Hydrogen (H_2) is a sustainable and long-term energy carrier with the capacity to meet growing global energy demands.[1,2] It can be applied across sectors such as transportation, industry, and heating systems. However, the volatile and flammable nature of hydrogen poses significant challenges, particularly in distribution via pipelines due to the risk of leakage.[3] Ammonia (NH_3) offers a promising alternative as a hydrogen carrier, with a high hydrogen content (17.6 wt%), carbon-free properties, and ease of storage at low pressure (~7.5 atm at 300 K).[4,5] The endothermic NH_3 cracking process can reliably generate hydrogen for clean energy technologies like fuel cells.[6] Despite this potential, the cost and low energy efficiency of current NH_3 cracking catalysts hinder their large-scale adoption.[5,7,8] Traditional catalysts, predominantly based on expensive late-transition metals like ruthenium, are unsuitable for widespread use.[9] Furthermore, current experimental studies lack sufficient depth to identify cost-effective alternatives to ruthenium.[10]

Materials and Methods

The samples were synthesized through a wet impregnation method, beginning from the precursors: ruthenium (III) chloride trihydrate, yttrium (III) nitrate hexahydrate, zirconium (IV) oxynitrate hydrate and strontium nitrate, supported on γ- Al_2O_3. Following dissolution in deionized water and vigorous stirring of the mixture and heating at 80°C for 6 hours, the impregnated supports were dried at 110°C for 12h, then calcined in air for 2h at 200°C and 3h at 550°C. Subsequently, the catalysts were reduced in hydrogen at 550°C for 3h. The characterization of the catalysts was conducted through the utilization of XRD, TEM, N_2-TPR, and NH_3-TPR techniques. The catalytic activity measurements for the decomposition of ammonia were evaluated in a quartz tubular reactor operating under atmospheric pressure and fed with a helium-ammonia mixture (2000 ppm NH_3) with a constant flow rate (100 mL/min). All experiments were conducted within the temperature range of 250 to 500°C, utilizing a catalyst loading of 100 mg.

Results and Discussion

The Ru content was halved and partially replaced with secondary elements to evaluate their impact on catalytic performance. To isolate the effect of the substitutions, the total metal loading was maintained at 4% across all samples. When Ru content was reduced to 2%, catalysts incorporating Y and Zr demonstrated the highest activity, achieving nearly 100% NH_3 conversion at 425°C. In contrast, Sr substitution led to a decline in catalytic efficiency, as active Ru sites were replaced by less

effective transition metal sites. Structural and electronic properties of Ru sites were unaffected, as indicated by the Arrhenius plots, which showed no change in apparent activation energy across the catalysts. The activation energy values (17.4–20.6 kcal/mol) align closely with those reported for Ru/Al_2O_3 catalysts in similar studies.[11]

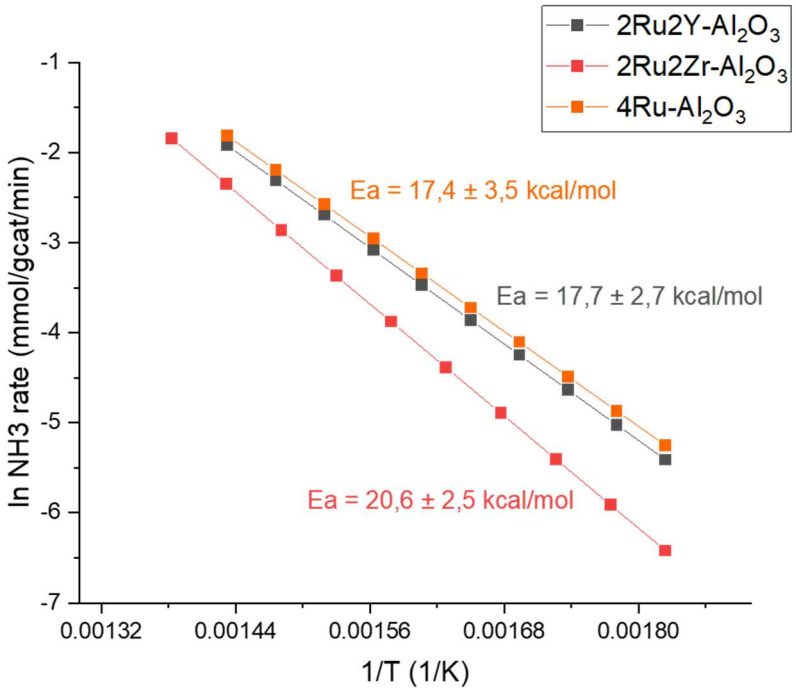


Figure 1. Arrhenius plot for RuY, RuZr and 4Ru. Experimental conditions: p=1 bar, NH3 concentration = 2000 ppm, total flow rate = 100 mL/min, catalyst amount = 100 mg.

References

1. A. Pareek, R. Dom, *Mater. Sci. Energy Technol.* **2020**, *3*, 319–327
2. H.A. Lara-García, J.A. Mendoza-Nieto, *Int. J. Hydrogen Energy* **2019**, *44*, 30062–30074
3. IEA, *The Future of Hydrogen: Seizing today's opportunities, Propos. Doc. Jpn. Pres. G20* (**2019**) *203*
4. G. Wang, A. Mitsos, *AIChE J.* **2017**, *63*, 1620–1637
5. A. Valera-Medina, R. Banares-Alcantara, *Elsevier* **2021**
6. S. Chiuta, R.C. Everson, *Int. J. Hydrogen Energy* **2013**, *38*, 14968–14991
7. K. Fothergill, S. Greenwood, *Ammonia to green hydrogen project, Feasibility Study* **2020**, *33*,1–70
8. O. Grasham, V. Dupont, *Energy Fuels* **2020**, *4*, 5835–5850
9. L. A. Parker, N. Richards, *Catalysis Letters* **2024**, 154, 1958-1969
10. Ganley, Jason C., *Catalysis Letters* **2004**, *96*, 117-122
11. T. V. Choudhary, C. Sivadinarayana, *Catalysis Letters* **2001**, *72*, 197-201

Acknowledgements

A. H. A Monteverde, C. Castelli and G. Cardolini Rizzo carried out this study within the National Recovery and Resilience Plan (PNRR) and received funding by the Italian Ministry of the Environment and Energy Security, project "Novel Materials for Hydrogen storage (NoMaH)", ID RSH2A_000035, CUP: F27G22000180006

Parametric investigation of an electrified steam methane reforming process using CFD modelling

Theodoros LYRAS [*,1], Panagiotis DROSATOS [1], Nikos NIKOLOPOULOS [1]

[1] *Centre for Research and Technology Hellas, 6th km Charilaou-Thermi Rd., 57001, Thessaloniki, Greece.*

** th.lyras@certh.gr*

Significance and Relevance

The present work introduces a Computational Fluid Dynamics (CFD) tool for modelling an electrified steam methane reforming (e-SMR) process. The intended use of the developed model is the evaluation and optimisation of e-SMR reactors. In this framework, the developed CFD models predict the performance of an electrically heated reactor unit within a broad spectrum of operating conditions. The resulting simulation data are presented in a comparative manner and provide a clear overview of the key operating parameters and their effect on the output of the e-SMR process.

- *Preferred and 2nd choice for the topic:* "Multiscale modeling and advanced simulation aspects" / "Catalysis to electrify the chemical production"
- *Preferred presentation*: Oral only

Introduction and Motivations

In 2022, more than 90% of the hydrogen produced in Europe was a product of a reforming process, [1] while globally, hydrogen production by methane-containing natural gas reforming is estimated to be around 48%.[2] Steam methane reforming (SMR) is an energy-intensive catalytic process, thus the efficient electrification of this process is of great importance for the decarbonisation of hydrogen production.[3] For that reason, a lot of research is conducted both on the development of more efficient e-SMR systems,[4,5] but also on the techno-economic viability of such solutions.[6] For enhancing the ability to assess and optimise such systems, the introduction of specialized numerical tools is crucial. The present work introduces a CFD-based model designed to numerically simulate, evaluate, and optimize e-SMR reactors.

Materials and Methods

A Computational Fluid Dynamics (CFD) model is developed to simulate the e-SMR process that takes place inside an experimental, electrically heated, FeCrAl reactor tube, partially coated with a Nickel-based catalytic washcoat.[7] The model is built in the ANSYS Fluent® environment and accounts for the conservation of mass, energy and momentum within the system. An in-house code is developed to describe the chemical kinetics and mass diffusivity within the catalytic washcoat. The developed functions describing the chemical kinetics are based on the work of Xu & Froment,[8] while the diffusivity model is based on the publication of Rostrup-Nielsen and Christiansen.[9] The model is validated against experimental data for a wide range of operating conditions in terms of mass flow rates and power load.[7] The validated model is used to predict the performance of a given system in the case of various operating conditions and catalytic properties. Eventually, the developed model can be effortlessly modified and used as an optimisation tool for reforming reactors.

Results and Discussion

The operating pressure of the unit, the mass flow rate of the methane mixture, the provided steam-to-fuel ratio, and the power supplied for heating the reactor are the key operating parameters examined in the CFD simulations. From the catalyst side, two main properties are investigated, namely the porosity and the average pore diameter of the catalytic washcoat. In total, twenty sets of operating conditions are simulated. For each set of conditions and properties, the resulting data are presented in terms of methane conversion, net power usage, temperature variation within the reactor domain

and species mole fraction distribution along the tube length, whereas the flow field and the pressure drop within the channel are also reported for each case. Indicative results from the numerical campaign can be found in **Figure 1**. The resulting data are presented in a comparative manner and provide a clear overview of the correlation between the operating parameters and the products of an e-SMR process. Since the model can be easily adapted and used with various reactor arrangements, it can function as an effective optimisation tool for compact e-SMR reactor for hydrogen production.

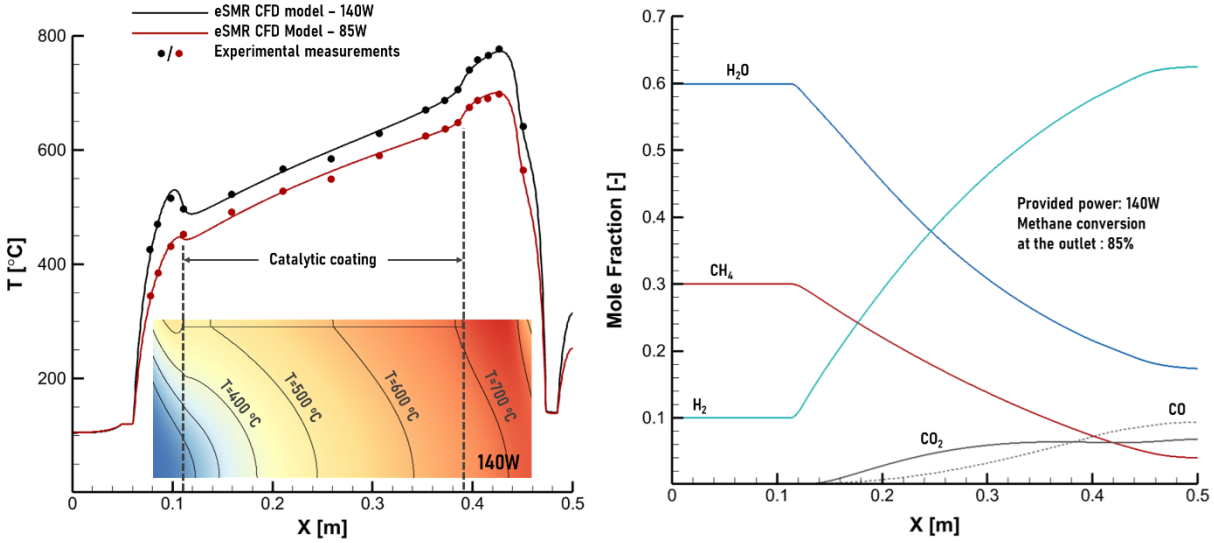


Figure 1. *Experimental measurements[7] and corresponding numerical predictions of the e-SMR CFD model for power load of 140 and 85W. A contour plot of the temperature of the reactor domain is presented on the bottom of the diagram (left). Line diagram of the evolution of the mole fractions of the reacting species along the reactor length, as measured at the axis of symmetry (right).*

References

1. Clean Hydrogen Monitor Report, https://hydrogeneurope.eu/, 2003.
2. M. Ji, J. Wang, International Journal of Hydrogen Energy, 2021, 46(78), 38612.
3. D. Maporti, S. Guffanti, F. Galli, R. Mocellin, G. Pauletto, Chemical Engineering Journal, 2024, 499, 156357.
4. S. Wismann, J. Engbaek, S. Vendelbo, F. Bendixen, W. Eriksen, K. Aasberg-Petersen, C. Frandsen, I. Chorkendorff, P. Mortensen, Science, 364(6442), 756.
5. D. Pashchenko, R. Mustafin, A. Mustafina, Energy, 2021, 237, 121624.
6. H. Song, Y. Liu, H. Bian, M. Shen, X. Lin, Energy Conversion and Management, 2022, 258, 115513.
7. S. Wismann, J. Engbaek, S. Vendelbo, W. Eriksen, C. Frandsen, P. Mortensen, I. Chorkendorff, 2019, Industrial and Engineering Chemistry Research, 58(51), 23380.
8. J. Xu, G. Froment, AIChE journal, 1989, 35(1), 88.
9. J. Rostrup-Nielsen, L. Christiansen, 2011, Concepts in syngas manufacture, World Scientific.

Acknowledgements

This work was supported by the European Union Project ERETECH, under the GA number 101058608. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or CINEA. Neither the European Union nor the granting authority can be held responsible for them.

Fully Renewable Diphenolic Acid Production in Batch and Continuous Reactors in the presence of new biomass-derived acid catalysts and LCA assessment of the entire process

Benedetta BERTINI[1], Domenico LICURSI[1], Francesco TADDEO[2], Alessandra SESSA[3], Nicola SCOTTI[4], Raffaele CUCCINIELLO[3], Vincenzo RUSSO[2], Anna Maria RASPOLLI GALLETTI[1], Claudia ANTONETTI[*,1]

[1]*University of Pisa, Department of Chemistry and Industrial Chemistry, Via G. Moruzzi 13, 56124 Pisa, Italy.*

[2]*University of Naples Federico II, Department of Chemical Sciences, Via Cintia, 80126 Naples, Italy.*

[3]*University of Salerno, Department of Chemistry and Biology, Via G. Paolo II 132, 84084 Fisciano, Italy.*

[4]*CNR, SCITEC "Giulio Natta", Via C. Golgi 19, 20133 Milano, Italy.*

** claudia.antonetti@unipi.it*

Significance and Relevance

The synthesis of a fully renewable diphenolic acid (DPA) represents a significant step forward as a "*green*" alternative to bisphenol A (BPA) for the production of epoxy resins and polycarbonates. This innovative process integrates levulinic acid (LA), phenol (PhOH) and catalysts derived from lignocellulosic biomass, making the entire production pathway renewable and environmentally friendly. In particular, in the presence of *ad-hoc* char-derived acid catalysts obtained from glucose and xylose, *p,p'*-DPA yields of about 20 mol% were achieved, paving the way for its fully sustainable production.

Preferred and 2nd choice for the topic: 1. Green chemistry and biomass transformation, renewable resources conversion; 2. Circular economy.
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster): Oral only

Introduction and Motivations

Nowadays, DPA is receiving significant relevance as an environmentally friendly alternative of BPA, due to its structural similarity and reduced environmental and toxicological impact.[1] The *p,p'*-DPA isomer, known for its promising properties, is traditionally synthesized through the condensation reaction between PhOH and LA in the presence of Brønsted acids catalysts, in particular mineral ones.[2] However, this approach leads to significant corrosion and difficult catalyst recycling. On this basis, the use of heterogeneous systems, especially those derived from renewable resources, is becoming crucial and in this context, the PRIN 2020 LEVANTE project aims to synthesize a fully renewable *p,p'*-DPA, in agreement with the principles of green chemistry. In this perspective, lignocellulosic waste biomasses represent promising renewable resources to be transformed into LA (cellulose and hemicellulose fractions) and into PhOH and substituted phenolic derivatives, such as catechol (lignin fraction). Additionally, the use of biomass-derived catalysts offers the opportunity to make the entire DPA synthesis fully renewable.[3] To achieve this goal, new *ad-hoc* acid catalysts were synthesized by sulfonating xylose- and glucose-derived hydrochars and tested for the selective production of *p,p'*-DPA and its derivative *p,p'*-DPAC (the corresponding DPA obtained from catechol) in batch and continuous reactors. The effects of main reaction parameters on the *p,p'*-DPA yield were investigated and optimized for both reactor configurations. Under the best reaction conditions, *p,p'*-DPA yields of about 23 mol% were reached in batch reactor and 12 mol% in continuous one, with ongoing efforts to improve the feasibility of *p,p'*-DPAC production. Simultaneously, a Life Cycle Assessment (LCA) was performed to compare the environmental impacts of this renewable DPA synthesis method with conventional mineral acid-based processes, aimed at the evaluation of the overall sustainability and environmental benefits of this investigated novel approach.

Materials and Methods

Ad-hoc char-derived acid catalysts (HTC-G-S and HTC-X-S from glucose and xylose respectively) were synthesized from glucose and xylose respectively, through a two-step procedure. This required a first hydrothermal carbonization step (HTC), carried out at 220 °C for 5 h with the starting biomass loading of 20 wt%, followed by a sulfonation functionalization carried out employing 15 mL of 96 wt%

H_2SO_4/g char. The synthesized catalysts were characterized by ultimate analysis, FT-IR, SEM, TGA, BET and Brønsted acidity.[3] In batch reactor, the reaction was performed in a pressure tube at 60-100 °C for 24-90 h under solvent-free conditions, whereas the continuous configuration consisted in a packed bed reactor made of stainless steel pipe (outer diameter ¼", length 30 cm) packed with the synthesized catalyst (0.5 g), feeding the LA/PhOH 1:2 solution in ethanol 1:5 via syringe pump. The reaction mixtures were analyzed by High-Performance Liquid Chromatography system, whereas the DPAC product was detected through quantitative Nuclear Magnetic Resonance. LCA analysis was performed adopting a comparative approach within the cradle-to-gate boundaries referring to the production of 1kg of *p,p'*-DPA (functional unit). The SimaPro software was used as the main tool and the ReCiPe method was selected to assess environmental impacts at both midpoint and endpoint level.

Results and Discussion

The synthesized HTC-G-S and HTC-X-S catalysts were preliminarily characterized, revealing an increase of sulfur content, due to the sulfonation treatment (1.23 – 1.13 wt% compared to < 0.1 wt% in the pristine samples), confirming the success of the derivatization procedure. At the same time, a notable increase of acidity (about 30-35 %) was observed, further highlighting their promising use in acid catalysis. Thus, the synthesized HTC-G-S and HTC-X-S catalysts were employed for the DPA synthesis in batch and continuous reactors, monitoring the kinetics (24-72h) at different temperatures and acidities (100 and 120 °C with molar ratio LA/H^+ of 3.4 and 6.8), adopting the LA/PhOH molar ratio of 1:4. These catalysts enabled us to obtain appreciable *p,p'*-DPA yields in batch processes, about 17-23 mol%, with high *p,p'*-DPA/*o,p'*-DPA molar ratios (≥ 16), even at reduced acidity (Figure 1A). These systems also allowed us to achieve *p,p'*-DPA yields between 8 and 12 mol% in continuous reactors. For comparison, the reaction conditions already optimized for PhOH were applied to catechol, thus confirming the effectiveness of the synthesized catalysts for the proposed application and their potential for synthesizing new DPA-derivatives. Finally, the LCA analysis demonstrated that this new process is competitive with traditional methods with strong mineral acids, showing that the use of these heterogeneous catalysts can reduce environmental impacts by enabling catalyst recycling and reuse across consecutive reaction cycles, thus simplifying the purification procedure.

In conclusion, in this research, the synthesis of a fully renewable DPA from biomass has been performed (Figure 1B), adopting a totally eco-sustainable perspective.

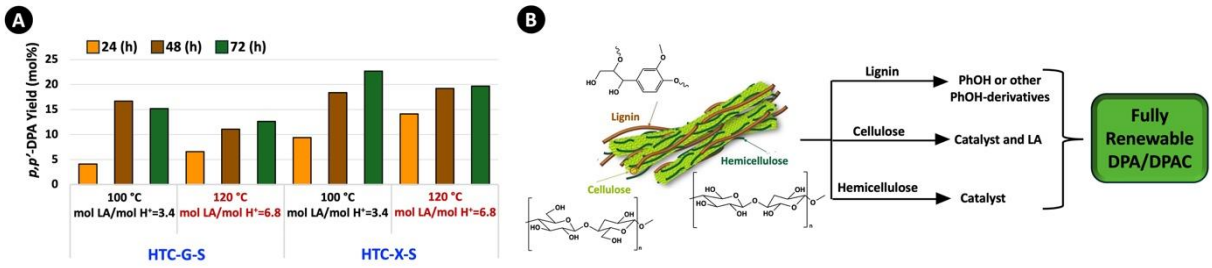


Figure 1 Catalytic results of the DPA synthesis in the presence of HTC-G-S and HTC-X-S catalysts (A) and fully renewable DPA synthesis from biomass (B)

References

1. L. Shen, J. Jiang, J. Liu, F. Fu, H. Diao, H. Liu, *Appl. Surf. Sci.* **2022,** *600*, 154152.
2. H.F. Liu, F.X. Zeng, L. Deng, B. Liao, H. Pang, Q.X. Guo, *Green Chem.* **2013,** *15,* 81.
3. D. Licursi, A.M. Raspolli Galletti, B. Bertini, L. Ardemani, N. Scotti, N. Di Fidio, S. Fulignati, C. Antonetti, *Sustain. Chem. Pharm.* **2023,** *35*, 101216.

Acknowledgements

The authors would like to thank the Italian Ministero dell'Istruzione, dell'Università e della Ricerca for funding the PRIN 2020 LEVANTE project "LEvulinic acid Valorization through Advanced Novel TEchnologies" (Progetti di Ricerca di Rilevante Interest Nazionale Bando 2020, 2020CZCJN7).

Heterogeneous catalysts based on hybrid POSS nanocages for sustainable applications

Michelangelo GRUTTADAURIA[*,1], Carmela APRILE[*,2], Francesco GIACALONE[*,1], Carla CALABRESE[*,3,§]
[1]*University of Palermo, Department of Biological, Chemical and Pharmaceutical Sciences and Technologies, Viale Delle Scienze, Ed. 17 90128, Palermo Italy.*
[2] *University of Namur, Department of Chemistry, Namur Institute of Structured Matter (NISM), 61 rue de Bruxelles, Namur 5000, Belgium.*
[3] *National Research Council of Italy, Institute for the Study of Nanostructured Materials (ISMN), Via Ugo La Malfa 153, 90146, Palermo, Italy.*
§ 1,2 former affiliations
** carla.calabrese@cnr.it*

Significance and Relevance

The critical need to reduce CO_2 emissions and improve the design of highly recyclable heterogeneous catalysts led us to the development of organic-inorganic hybrid materials from polyhedral oligomeric silsesquioxanes (POSS). In this scenario, we address the application of POSS nanocages as heterogeneous catalysts able to promote CO_2 conversion into cyclic carbonates and C-C cross-coupling reactions, among others. A series of imidazolium-functionalised POSS nanocages was grafted onto silica supports to be used as both organocatalysts and stabilizing supports for palladium-based active species. The proposed materials showed promising catalytic features combined with a wide versatility.

Preferred and 2nd choice for the topic: CO2 utilization and recycling, Green chemistry and biomass transformation, renewable resources conversion
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The design of functional heterogeneous catalysts is part of the transition process toward a more sustainable economy. The huge demand for novel hybrid materials prompted us to focus on the design of modular and efficient synthetic strategies by using imidazolium-modified POSS as building blocks for the preparation of nanocatalysts with tunable applications.[1]

Results and Discussion

Imidazolium-functionalised POSS hybrid molecules were grafted onto silica supports to be used as heterogeneous catalysts for sustainable applications. The proposed materials were prepared *via* a modular synthetic procedure to obtain a high local concentration spots of imidazolium surrounding the POSS nanocage. CO_2 conversion by reaction with epoxides was carried out under solvent- and metal-free reaction conditions showing a full selectivity toward the corresponding cyclic carbonate.[2] On the other hand, imidazolium-modified POSS nanocages grafted onto SiO_2 were used as solid supports for palladium active species in order to catalyse Suzuki-Miyaura, Heck cross-coupling reactions,[3] and the oxidative carbonylation of β-amino alcohols. All the catalysts were fully characterised, easily recycled from the reaction media, and tested with a broad scope of substrates. The synergistic features of the proposed materials can be improved and extended to further catalytic applications. The huge versatility of POSS nanostructures arises from the easy tunability of peripheral organic moieties combined with the high thermal and chemical stability of the inner inorganic core.

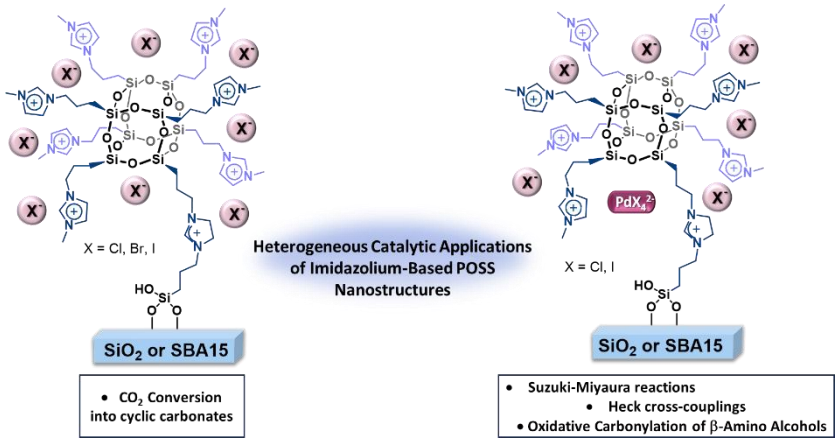


Figure 1 Imidazolium-modified POSS nanocages and their applications in catalysis.

References

1. C. Calabrese, C. Aprile, M. Gruttadauria, F. Giacalone, *Catal. Sci. Technol.*, **2020**, *10*, 7415.
2. C. Calabrese, L. F. Liotta, F. Giacalone, M. Gruttadauria, C. Aprile, *ChemCatChem*, **2019**, *11*, 560.
3. C. Calabrese, V. Campisciano, F. Siragusa, L. F. Liotta, C. Aprile, M. Gruttadauria, F. Giacalone, *Adv. Synth. Catal.*, **2019**, *361*, 3758.

Acknowledgements

The University of Palermo and the University of Namur are gratefully acknowledged for a co-funded research activity. The authors are thankful to PC2 (Plateforme Technologique Physico-Chemical Characterization), MORPH-IM (Morphology & Imaging) and SIAM (Synthesis, Irradiation & Analysis of Materials) technology platforms located at the University of Namur. The National Research Council of Italy (ISMN-CNR) is warmly acknowledged for complementary characterisations whereas the University of Calabria is warmly acknowledged for carbonylation catalytic tests.

GASIFICATION OF RESIDUAL BIOMASS IN A ROTARY KILN REACTOR INTEGRATED WITH RADIO FREQUENCY PLASMA TORCH

Enrico CATIZZONE[1], Cesare FREDA[2], Antonio VILLONE[2], Assunta ROMANELLI[2], Giacinto CORNACCHIA[2]
[1]*Chemical Engineering Catalysis and Sustainable Processes Laboratory, University of Calabria, Rende, Italy.*
[2]*Laboratory of Thermochemical processes for waste and biomass, Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA), Trisaia Research Center, Rotondella, Italy.*

** enrico.catizzone@unical.it*

Significance and Relevance

Process intensification of biomass gasification is of paramount importance to improve the producer gas quality, pushing towards a higher production of hydrogen. Low hydrogen content and the presence of tar are the main challenges to be addressed. At this regard, for the first time, a rotary kiln gasifier is integrated with a radio frequency plasma torch. The proposed integration significantly improves both the hydrogen yield and the H_2-to-CO ratio, with no gravimetric tar.

Introduction and Motivations

Biomass conversion towards chemical intermediates or fuels is considered as one of the most important decarbonization strategy[1]. At this regard, the research and development activities carried out on biomass gasification are focused, from a technological point of view, on the tar reduction as well on the increase of hydrogen production. Tar as well as low hydrogen content is recognized as the "Achilles heel" of the gasification. To date very limited literature was recovered about biomass gasification in rotary kiln[2,3]. The aim of this work is to demonstrate the suitability of the integration of rotary kiln with a plasma torch device, able to produce a clean syngas with high hydrogen content, also under not optimal conditions for air gasification, i.e. 650 °C and an equivalence ratio equals to 0.15.

Materials and Methods

Residual lignocellulosic biomass is used as feedstock for a gasification process carried out with air as gasifying agent. A 10 kW_{th}-rotary kiln was used as gasifier. The effect of gasification temperature on the producer gas quality was studied in the range 650-900 °C. The biomass is fed with a flowrate set at 190 g/h, 450 g/h or 900 g/h. Post-gasification treatment was assessed by considering both conventional thermal unit (up to 1100 °C) and plasma-based unit adopting a radio frequency plasma torch.

Results and Discussion

On the basis of nitrogen-free composition, the trends indicate that both hydrogen and carbon monoxide content increase as the gasification temperature increases, while an opposite trend is observed for carbon dioxide and methane. Higher temperature favors endothermic reactions such as Boudouard, reverse water gas shift, reforming (steam/dry) and cracking of hydrocarbons, while exothermic reactions, such as methanation is hindered. Due to an increase of endothermic reactions both hydrogen and carbon monoxide concentration increase. Endothermic reactions, such as Boudouard and reverse water gas shift and dry reforming occur with carbon dioxide consumption that can be the cause of decrease of carbon dioxide concentration in the syngas by increasing the gasification temperature. The beneficial effect of gasification temperature on both syngas yield and syngas lower heating value has a direct effect on cold gas efficiency, that proportionally increases from about 20% to about 64% in the investigated temperature range, as reported in Figure 1.

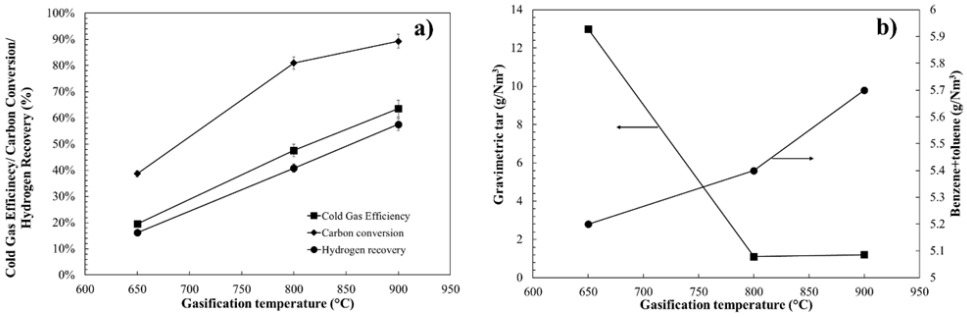


Figure 1 – Effect of gasification temperature on gasification performances

As a rule, the increase of biomass reactivity pushed by temperature increase favor the conversion of carbon and hydrogen, from solid phase to gas phase. In fact, carbon conversion increases from about 39% to about 89% by increasing the temperature from 650°C to 900°C. Hydrogen recovery linearly depends on the temperature, under the investigated conditions.

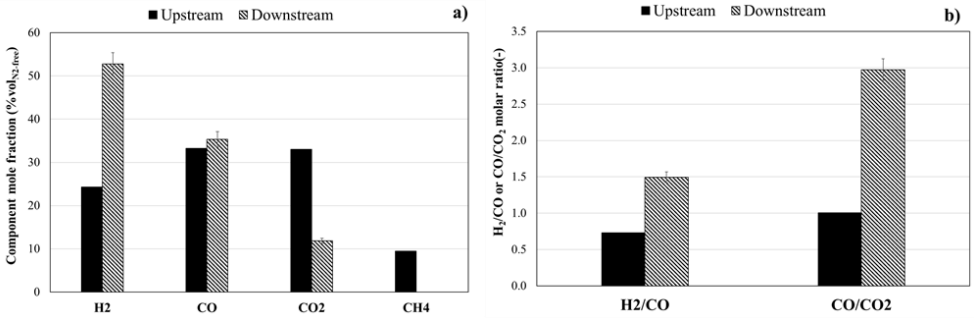


Figure 2 – Syngas composition (a) and H_2/CO and CO/CO molar ratio (b) upstream and downstream radio frequency plasma torch during the following gasification tests: 450 g/h, 650°C, e.r. 0.15

Figure 2-a shows the effect of post-gasification treatment on syngas composition calculated on nitrogen-free basis. It is noteworthy the strongly reduction of methane in the syngas, whose downstream radiofrequency plasma torch concentration is lower than the limit of detection. The elimination of methane from syngas can be caused by several reactions that are favored at high temperature, such as steam and dry reforming, as well as thermal cracking.

Furthermore, radiofrequency plasma torch treatment causes an undoubtedly increase of both hydrogen and carbon monoxide concentration, with a parallel decrease of carbon dioxide concentration. These changes as an effect in terms of both H_2-to-CO and CO-to-CO_2 molar ratio, as depicted in Figure 2-b. The ratio between the generated hydrogen and the generated carbon monoxide is higher than one, i.e. about 2.3, indicating that steam reforming of hydrocarbons could be the predominant reaction. Since a carbon dioxide flowrate reduction was observed, dry reforming and/or reverse water gas shift probably occur in the system

References

1. V. Ashokkumar, et al. *Fuel* **2024**, *365*, 130751.
2. C. Freda et al., *Fuel* **2018**, *218*, 88.
3. C. Freda et al., *Res. Eng.* **2024**, *21*, 101763.

Acknowledgements

This project belongs to the European Union's Horizon 2020 research and innovation program, under grant agreement No. 101006656 GICO Project.This work reflects only the authors' views and opinions, neither the Ministry for University and Research nor the European Commission can be considered responsible for them.

Surface Carbon Formation and its Impact on Methane Dry Reforming Kinetics on Rhodium-Based Catalysts by Operando Raman Spectroscopy

Riccardo Colombo[1], Gianluca Moroni[1], Chiara Negri[1], Matteo Monai[2], Bert M. Weckhuysen[2], Matteo Maestri[1]*

[1]*Politecnico di Milano, Department of Energy, LCCP group, via La Masa 34, 20156 Milan, Italy*
[2]*Utrecht University, Inorganic Chemistry and Catalysis Group, Universiteitsweg 99, Utrecht, The Netherlands*
matteo.maestri@polimi.it

Significance and Relevance

A mechanism for carbon deposition and its impact on Methane Dry Reforming (MDR) kinetics using rhodium-based catalysts is presented. By integrating Raman spectroscopy with kinetic analysis in an operando-annular reactor under strict chemical conditions, we discovered that carbon deposition on a $Rh/\alpha\text{-}Al_2O_3$ catalyst follows a nucleation-growth mechanism strongly influenced by the CO_2/CH_4 ratio and the CH_4 concentration. This work elucidates the spatiotemporal development of carbon aggregates on the catalyst surface and their effects on catalytic performances. Furthermore, these findings prove that CO_2 influence on MDR kinetics is just an indirect result of carbon accumulation.

Preferred and 2nd choice for the topic: 1st CO_2 utilization and recycling, 2nd Fundamental advances in understanding catalysis
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Methane Dry Reforming reaction (MDR) is a promising route for biogas valorization. Nevertheless, MDR industrial scalability is constrained by catalyst deactivation due to carbon deposition, a phenomenon with mechanisms and kinetic implications still under debate.[1,2] In our investigation, we have combined kinetic measurements in an annular reactor, time-resolved and spatially-resolved operando Raman spectroscopy to shed light on the carbon formation pathway and its kinetic consequences during MDR over Rh-based catalysts.

Materials and Methods

MDR catalytic tests have been performed employing an operando-annular reactor in conjunction with Raman spectroscopy. The reactor consists of a hollow alumina tube as structural support sealed at one end and coaxially inserted in an optical-quality quartz tube. The catalyst (4 wt.% $Rh/\alpha\text{-}Al_2O_3$), coated as a thin layer (thickness 10-30 µm, length 20 mm) on the external surface of the alumina tube, was prepared via dry impregnation of the $\alpha\text{-}Al_2O_3$ support with a solution of the active phase precursor ($Rh(NO_3)_3$). A sapphire window is present in correspondence to the catalytic bed to collect both time-resolved and spatially-resolved operando Raman spectra through a laser probe supported on a motorized moving stage. The Raman measurements are performed by a JASCO ® NRS-4100 spectrometer equipped with a Coherent® Sapphire SF488 laser (488 nm) as an excitation source.

Results and Discussion

Several tests at different co-reactant-to-methane ratios (CO_2/CH_4 between 2 and 0.25) and inlet CH_4 molar fractions (8 vol.% and 1 vol.%) have been performed at 600°C and atmospheric pressure to investigate the kinetic role of CO_2, the mechanism of carbon formation over $Rh/\alpha\text{-}Al_2O_3$ catalyst and how these two are correlated during MDR.[3] The experimental evidence (Figure 1.a) shows that when $CO_2/CH_4 \geq 1$ methane conversion curves undergo an initial decline over time, with a slope notably influenced by the co-reactant-to-methane ratio, followed by an apparent conversion stabilization at higher times. For tests at inlet CH_4 8 vol.% and ratios equal to 2 and 3 the initial slope of the curve is lower than the one observed for ratio equal to 1, while for ratios below the unity (e.g., 0.5 and 0.25) the curve is quite flat at a stationary value. As shown in Figure 1.b, Raman spectra acquired in over-stoichiometric conditions show no presence of carbon peaks (i.e. G and D peaks) over 24 h. Conversely, at stoichiometric ratio, Raman spectra revealed the formation of carbonaceous structures after 3 h of

reaction, while for sub-stoichiometric ratios Raman spectra highlight the presence of carbon peaks already after 5 minutes from the beginning of the catalytic test.

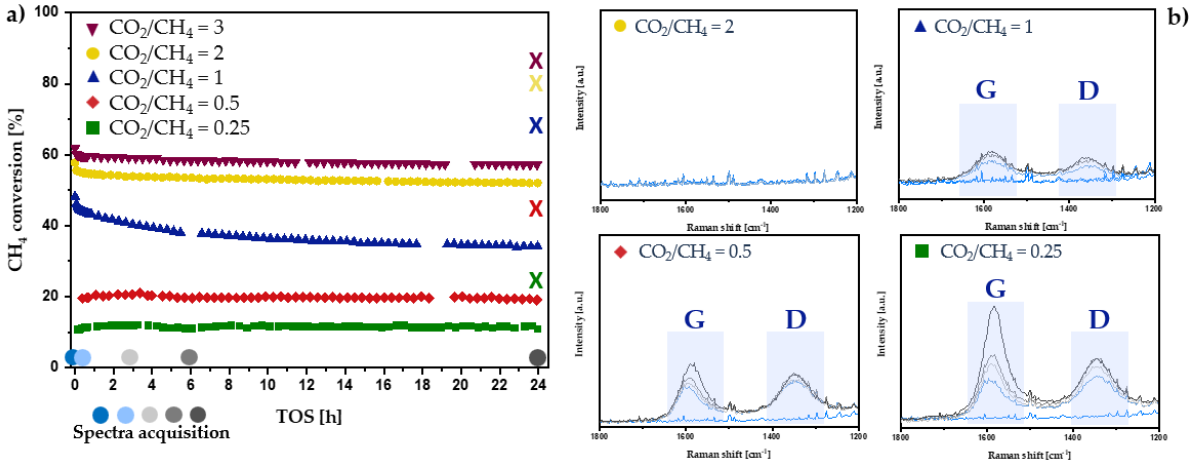


Figure 1. a) Experimental (symbol) and equilibrium ("X" symbol) methane conversion at different CO_2/CH_4 ratios for MDR on 4% Rh/Al_2O_3 catalyst at CH_4 = 8 vol.% during 24 h tests. T = 600°C, P = 1 atm, GHSV = 1.4x10^6 NL/kg_{cat}/h; b) Raman spectra acquired before the reaction, after 5 min, 3 h, 6 h and 24 h.

Our findings indicate that the co-reactant concentration does not significantly alter the kinetics of MDR at the start of the reaction (TOS = 0 h). However, carbon deposition markedly impacts catalyst stability and activity. The deposition process, characterized by a longer timescale than the turnover rate, is strongly dependent on the CO_2/CH_4 ratio. Specifically, at a CO_2/CH_4 ratio of 1 or lower, carbon deposition is evident within 24 hours of operation. As proposed in Figure 2, adsorbed carbon (C*) and CH_x* species can follow two possible routes: under CO_2-rich conditions (i.e. $CO_2/CH_4 > 1$), they tend to follow preferentially Route 1 leading to CO formation; instead, in a CO_2-deficient environment, these species start to form solid carbon deposits via Route 2. The resulting carbon aggregates decrease the availability of Rh surface, leading to deactivation and providing an apparent kinetic dependence on CO_2. Moreover, spatially-resolved operando Raman spectra has unveiled a descending trend of carbon deposits along the reactor axial coordinate, while tests performed with the addition of a small fraction of O_2 (0.8 vol.%) proved to inhibit carbon species deposition and growth.

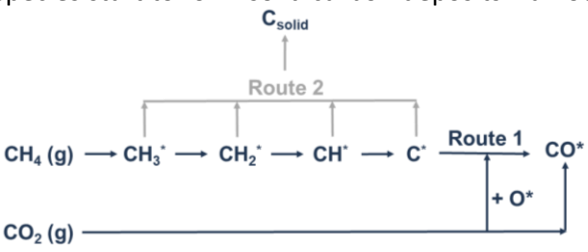


Figure 2. Proposed pathway for C-species formation

All in all, this work highlights the pivotal role of a multi-technique approach in deepening our understanding of catalytic processes, especially when intrinsic kinetics are obscured by deactivation.

References

1. J. Wei, E. Iglesia, J. Catal. **2004**, 225, 116–127
2. A. Donazzi, A. Beretta, G. Groppi, P. Forzatti, J. Catal.**2008**, 255, 259-268
3. R. Colombo, G. Moroni, C. Negri, G. Delen, M. Monai, A. Donazzi, B.M. Weckhuysen, M. Maestri, Angew. Chem. Int. Ed. **2024,** 136, e202408668

Acknowledgements

Financial support from the European Research Council (Grant 677423) and the National Recovery and ResiliencePlan (NRRP), Mission 4 Component 2 Investment 1.3 - Call for tender No.1561 of 11.10. 2022 of Ministero dell'Univer-sità e della Ricerca (MUR); funded by the European Union-NextGenerationEU-Award Number: Project codePE0000021, Concession Decree No.1561 of 11.10. 2022 adopted by Ministero dell'Università e della Ricerca (MUR), CUP D43C22003090001, according to attachment of Decree No. 1561/2022, Project title "Network 4 EnergySustainable Transition-NEST".

Valorization of different organic waste sources for electrochemical applications: Process and life cycle assessment

E. Petri[1], S. El Yamani[2,3], F. Capodarca[1], A. Primante[2,3], A. Contin[2.3], F. Soavi[1,3]*

[1]Dept. of Chemistry "Giacomo Ciamician", University of Bologna, Via Selmi 2, 40126, Bologna, Italy
[2] Dept. of Physics and Astronomy "Augusto Righi", University of Bologna, Viale Berti Pichat 6/2, 40127, Bologna
[3]Centre for the Environment, Energy, and Sea - Interdepartmental Centre for Industrial Research in Renewable Resources, Environment, Sea and Energy (CIRI-FRAME), University of Bologna, Viale Ciro Menotti 48, 48122, Marina di Ravenna, Italy

email: francesca.soavi@unibo.it

Significance and Relevance

In recent years, biochar produced through the pyrolysis and activation of biomass has emerged as a promising material for various electrochemical systems, including fuel cells, redox flow batteries and supercapacitors. Its production lines up with global efforts to move towards sustainable energy solutions by integrating renewable and waste-derived materials into advanced technologies. Moreover, biochar offers the potential to mitigate climate change by sequestering CO_2 and substituting high-emission, fossil-based products, thereby contributing to a more circular economy.

Preferred topic: Green chemistry and biomass transformation, renewable resources conversion
Second choice: Circular economy
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The growing demand for sustainable electrochemical energy storage and conversion systems has driven interest in the valorization of organic waste as a resource for innovative materials. Biomass, such as lignin and vine prunings, represents an abundant and renewable European feedstock for biochar production, which can be tailored for applications in energy storage devices. The optimization of biochar's porosity through pyrolysis and activation processes (e.g., using $KHCO_3$) enhances its electrochemical performance and adds value to the battery value chain. Additionally, valorizing waste-derived materials not only reduces environmental burden but also opens pathways for energy recovery and resource efficiency. Evaluating the environmental impacts of the proposed activated biochar production process through a life cycle assessment (LCA) further supports its viability as a sustainable solution[2].

Materials and Methods

Biochar was produced on a gram scale from organic wastes, such as lignin and vine prunings, via pyrolysis and chemical activation. Pyrolysis conditions were optimized to enhance porosity, with potassium bicarbonate ($KHCO_3$) used as a mild activating agent to increase surface area. The materials were characterized using scanning electron microscope (SEM), thermogravimetric analysis (TGA), nitrogen adsorption, elemental analysis and Raman spectroscopy. Pyrolysis by-products were evaluated for thermal energy potential, while a life cycle assessment (LCA) analyzed the environmental impacts, considering energy and material recovery and the integration of renewable energy.

Results and Discussion

The tailored pyrolysis and activation processes successfully produced biochar with optimized porosity, which is suitable for use in energy storage applications. Preliminary analyses indicate significant improvements in the material's electrochemical properties, making it a viable candidate for ORR and HER in fuel cells (inorganic and biological), as well as in vanadium redox flow batteries, supercapacitors and other energy storage systems. The evaluation of pyrolysis by-products revealed their potential for thermal energy recovery, contributing to the overall sustainability of the process. The life cycle assessment highlighted the environmental benefits of this approach, particularly in terms of CO_2 sequestration, reduced reliance on fossil-based products, and effective waste valorization. These findings underscore the feasibility and ecological advantages of integrating biochar into the energy storage value chain.

References

1. E. Petri, E. Heigl, A. Fasolini, L. Zeilerbauer, M. Giovannucci, Y. Küçükağa, C. Torri, F. Basile, F. Soavi. *Carbon*, **2024**, 226, 119-221.
2. M. Liu, Z. Xiang, H. Deng, K. Wan, Q. Liu, J.Piao, Y. Zheng, Z. Liang. *Journal of The Electrochemical Society,* **2016**, 163 (10), H937-H942.
3. L.J.R. Nunes, A.M. Rodrigues, J.C.O Matias, A.I.Ferraz. Rodrigues. *Agriculture* **2021**, *11*, 489.

Acknowledgements

This work was supported by the MIAMI Project 2022-2025 - Italian Minister for Ecological Transition, MiTE codice proposta CSEAA_00014

Bimetallic Platinum-Rhenium Catalysts: Enhancing Hydrogen Storage Efficiency through Material Optimization and Synthesis Modification

Elisabeth HERZINGER[1], Hannah PARK[1], Jennifer WEIMANN[1], Moritz WOLF[*,1,2]
[1] *Karlsruhe Institute of Technology (KIT), Institute of Catalysis Research and Technology (IKFT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.*
[2] *Karlsruhe Institute of Technology (KIT), Engler-Bunte-Institut (EBI), Engler-Bunte-Ring 1, 76131 Karlsruhe, Germany.*
** moritz.wolf@kit.edu*

Significance and Relevance

Dehydrogenation performance and productivity of Pt-Re catalysts are significantly influenced by the support material's composition, morphology, and surface chemistry. Novel insights include the identification of charge effects and interactions between the precursors of the two metals and between metal precursors and support material as critical factors. Additionally, the research highlights the impact of metal loading and synthesis procedures on catalyst activity, providing a comprehensive understanding of the optimization of these variables to enhance the hydrogen storage efficiency in LOHC systems.

Preferred and 2nd choice for the topic: Fundamental advances in understanding catalysis or H_2 storage and transportation
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Hydrogen as an energy carrier offers many benefits for the environment, energy security, economy, and end users.[1] However, cost-effective, compact, safe, and convenient storage of hydrogen are essential for large-scale implementation. Further, the volumetric energy density of hydrogen is low compared to other energy carriers.[2] One approach to address this challenge is the use of liquid organic hydrogen carriers (LOHCs) for chemical hydrogen storage. LOHCs are liquids that can chemically bind hydrogen in a reversible manner, which allows for long-term storage and safe transportation of hydrogen under ambient conditions.[3,4] Benzyltoluene/perhydro benzyltoluene (H0-BT/H12-BT) is a technical relevant LOHC system that is thermally stable, has a low toxicity, and has wide liquid range. It has a hydrogen storage capacity of 6.2 wt.%, which is equivalent to 2.1 kWh kg^{-1} or 1.9 kWh L^{-1}.[5] However, to maximize the hydrogen storage capacity and the number of repeated loading and unloading cycles via catalytic hydrogenation and dehydrogenation, respectively, a superior catalyst selectivity and high conversions are of utmost importance. We recently proposed the use of a bimetallic platinum-rhenium catalyst system, which shows particularly promising characteristics and is therefore an attractive subject for further research.[6]

Materials and Methods

In this study, the influence of support material and synthesis procedure on the dehydrogenation activity of bimetallic platinum-rhenium (Pt-Re) catalyst systems is investigated. Therefore, a range of supported Pt-Re catalysts were prepared by wet impregnation with strong electronic adsorption and the resulting catalysts as well as the bare support materials were thoroughly characterized by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray diffraction (XRD), transmission electron microscopy (TEM) and N_2 physisorption. Porous Al_2O_3 was used as catalyst support while the boehmite precursor and different calcination temperatures represent a first parameter variation. Further, the procedure for wet impregnation was altered, e.g. by multiple consecutive impregnation steps or by varying the order of the metal precursors applied. Dehydrogenation activity was then evaluated in semi-batch laboratory-scale dehydrogenation experiments to compare key performance indicators, such as the degree of dehydrogenation (DoDH) of perhydro benzyltoluene and the platinum-based productivity of the catalysts.

Results and Discussion

The dehydrogenation performance and catalyst productivity of the prepared catalysts strongly depends on the utilized supports. These results indicate that the composition, morphology and surface chemistry of the support significantly influence the catalyst activity. This may be linked to charge effects related to the point of zero charge of the support material and the charge of the applied metal precursors. Furthermore, a strong correlation with the metal loading and the synthesis procedure (Figure 1) could be observed. Insufficient distribution of the active metal over the support surface as well as strong interaction with material additives might hamper the catalysts activity. Morphological differences in the support materials, such as mean pore diameter and specific surface area, can additionally influence the activity, for example via pore diffusion limitations. In general, the activity of supported catalysts is based on a complex interplay of various factors, which are extensively examined to provide a better understanding of the underlying effects.

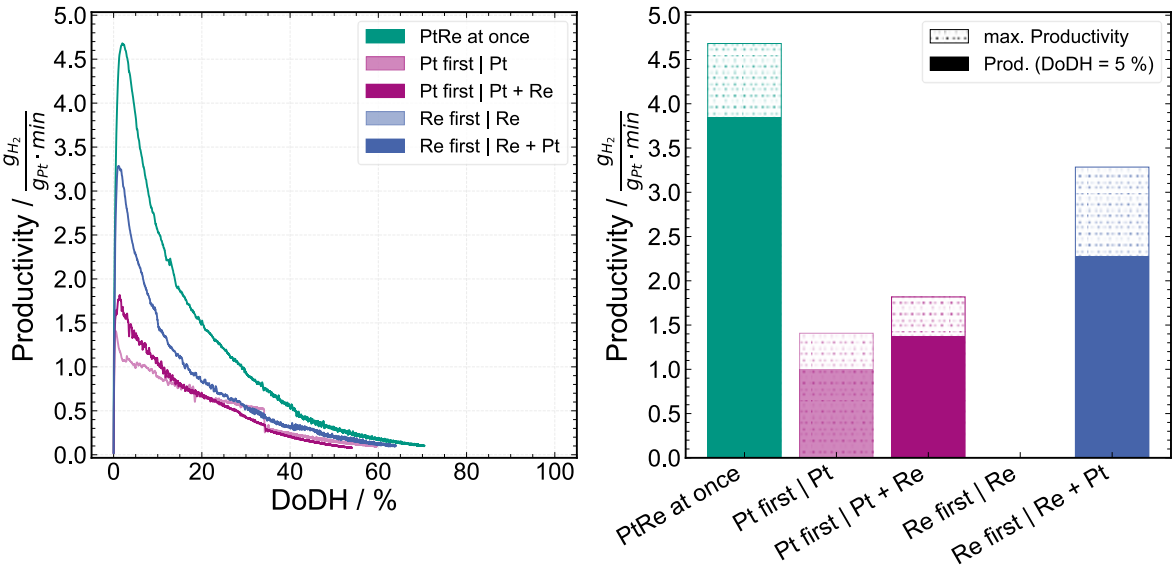


Figure 1: Productivity (left) and maximum productivity as well as productivity at a DoDH of 5% (right) during semi-batch dehydrogenation of perhydro benzyltoluene using Pt-Re/Al_2O_3 catalysts prepared by one impregnation step or two consecutive impregnation steps

The herein presented study provides fundamental insights into the performance of supported bimetallic platinum-based catalysts as a function of the structure and type of utilized support material as well as synthesis procedure. It especially highlights the importance of understanding how different factors can affect synthesis and catalyst activity in order to develop more efficient systems in the future.

References

1. J.O. Abe, A.P.I. Popoola, E. Ajenifuja, O.M. Popoola, *Int. J. Hydrog. Energy* **2019**, *44*, 15072
2. N. Armaroli, V. Balzani, *ChemSusChem* **2011**, *4*, 21
3. P. Preuster, C. Papp, P. Wasserscheid, *Acc. Chem. Res.* **2017**, *50*, 74
4. E. Herzinger, M. Wolf, *Chem. Ing. Tech.* **2024**, *96*, 65.
5. T. Rüde, S. Dürr, P. Preuster, M. Wolf, P. Wasserscheid, *Sustain. Energy Fuels* **2022**, *6*, 1541
6. D. Strauch, P. Weiner, B. B. Sarma, A. Körner, E. Herzinger, P. Wolf, A. Zimina, A. Hutzler, D. E. Doronkin, J.-D. Grunwaldt P. Wasserscheid, M. Wolf, *Catal. Sci. Technol.* **2024**, *7*, 1775.

Acknowledgements

The authors would like to thank the Helmholtz Research Program “Materials and Technology for the Energy Transition (MTET), Topic 3: Chemical Energy Carriers” for financial support.

Spark-ablated metal nanoparticle catalysts supported on TiO_2 for CO_2 methanation

Plaifa HONGMANOROM[1], Damien P. DEBECKER[*,1]
[1]*Institute of Condensed Matter and Nanoscience, UCLouvain, Place Louis Pasteur 1, Louvain-La-Neuve, Belgium.*
** damien.debecker@uclouvain.be*

Significance and Relevance

We report the first synthesis of a powdery heterogeneous catalyst using spark ablation technology.[1] A spark nanoparticle generator is modified to allow a direct deposition onto pulverulent materials. The concept relies on the aerosolization of a powder, which is gas-transported and injected in the path of metal nanoparticle formation. Herein, TiO_2 powder is used as the catalyst support, while Ni or Ru electrodes are used to generate Ni or Ru nanoparticles as the active phase. The resulting Ni/TiO_2 and Ru/TiO_2 catalysts are readily active in the hydrogenation of CO_2 to CH_4.

Preferred topic and 2nd choice for the topic: "CO_2 utilization and recycling" and "Fundamental advances in understanding catalysis"
Preferred presentation: Oral only

Introduction and Motivations

Spark ablation is a compelling alternative to traditional wet chemical methods, primed to reduced environmental impact (i.e., no use of solvents, precursors, salts, ligands, or high-temperature treatments). It was developed to generate nanoparticles, using electrical discharges between two electrodes of a target material in inert gas flow. This physical process yields metal particles in the 1-10 nm size range. The well-controlled deposition of generated metal nanoparticles onto flat surfaces has been well documented.[2, 3] Yet, for heterogeneous catalysis, powdery materials are needed.

Materials and Methods

In Figure 1, TiO_2 P25 powder was aerosolized from a mechanically vibrating reservoir by a 4-jet vortex fed with N_2. The aerosolized powder was transported through a venturi for de-agglomeration before injection into the spark generator. Sparks generated between the Ni or Ru electrodes produced Ni or Ru clusters, which were carried by N_2 to form Ni or Ru nanoparticles deposited onto TiO_2 particles. The resulting Ni/TiO_2 or Ru/TiO_2 catalysts were collected on filter paper.

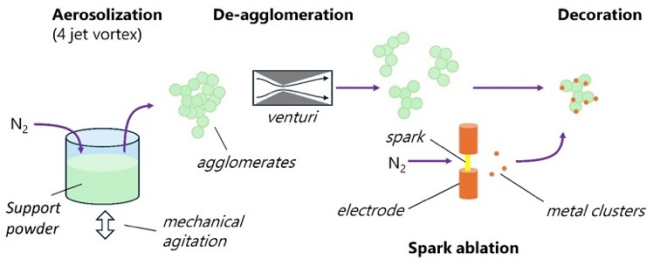


Figure 1. Schematic view on the set-up used to prepare powdery Ni/TiO_2 and Ru/TiO_2 catalysts.

Results and Discussion

The pristine TiO_2 support and the as-prepared Ni/TiO_2 catalyst exhibit a H3-type hysteresis loop, resulting from the interparticle voids in the loose aggregates of non-porous TiO_2 particles. The diffractograms of the TiO_2 support and the as-prepared Ni/TiO_2 catalyst are presented in Figure 2 (a). After Ni loading (2.3 wt% determined by ICP-AES), the TiO_2 diffraction peaks are unchanged in positions and width, which suggests that TiO_2 crystallites are unaffected by the catalyst preparation. Additionally, the main diffraction peaks of Ni ($2\theta = 44.6°$) or NiO ($2\theta = 43.1°$) crystalline phases are not detectable in the XRD pattern of the as-prepared Ni/TiO_2 catalyst, excluding the presence of Ni-based crystallites larger than 5 nm. HRTEM image (Figure 3(a)) further confirms this observation, showing small Ni nanoparticles (<5 nm) well-dispersed on TiO_2 and revealing the lattice fringes with inter-planar

distances of 2.0-2.1 Å and 2.35-2.45 Å, corresponding to the (111) crystal plane of cubic Ni and NiO, respectively. It should be noted that the homogeneity of the deposit is still not optimal, as some "floating" Ni/NiO nanoparticles can also be observed, not being in contact with TiO_2 support, in Figure 3(b). Despite no interaction with TiO_2 support, these nanoparticles are very small (<5 nm). Although the Ni loading, Ni particle size and metal-support interaction have not been fully optimized, the Ni/TiO_2 catalyst achieves satisfactory CO_2 conversion of 53% and CH_4 selectivity of 76% at 400°C, as shown in Figure 2(b). After the reaction, HRTEM image (Figure 3(c)) shows that small Ni nanoparticles (a few nanometer), well-dispersed on TiO_2 support, remain stabilized after reductive pretreatment and subsequent reaction. Nevertheless, few large particles (50-80 nm) can also be found in Figure 3(d), likely stemming from the sintering of "floating" Ni nanoparticles without interaction with TiO_2. The presence of few large Ni nanoparticles is consistent with the small and relatively narrow XRD peak at 44.6° of the spent Ni/TiO_2 catalyst in Figure 2(a).

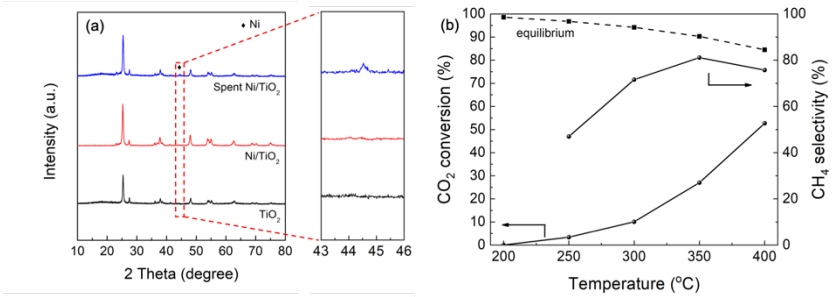


Figure 2. (a) XRD patterns of the TiO_2 support, as-prepared Ni/TiO_2 catalyst and spent Ni/TiO_2 catalyst. (b) CO_2 conversion and CH_4 selectivity of Ni/TiO_2 catalyst as a function of temperature.

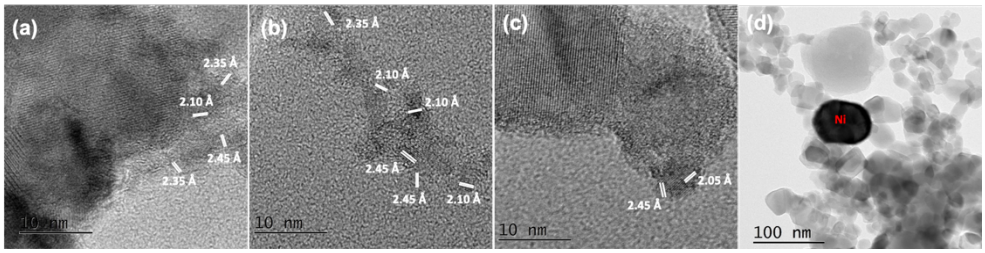


Figure 3. TEM images of (a) and (b) the as-prepared Ni/TiO_2 catalyst and (c) and (d) the spent Ni/TiO_2 catalyst.

The homogeneity of deposition could be further improved by improving the design of the mixing zone and better controlling the powder aerosolization. Additionally, the scope could be expanded to other metals (e.g., Ru, Rh, Pd, Co, and Fe), which have been reported as active and selective metal catalysts for CO_2 methanation. Currently, Ru electrodes are used to generate Ru nanoparticles deposited on TiO_2 powder. The resulting Ru/TiO_2 catalyst demonstrates promising catalytic performance, achieving 53% CO_2 conversion and 100% CH_4 selectivity at 300 °C.

References

1. D.P. Debecker, P. Hongmanorom, T.V. Pfeiffer, B. Zijlstra, Y. Zhao, S. Casale, C. Sassoye, *Chem. Commun.* **2024**, *60*, 11076.
2. T.V. Pfeiffer, J. Feng, A. Schmidt-Ott, *Adv. Powder Technol.* **2014**, *25*, 56.
3. S. Drdova, M. Gao, O. Sambalova, R. Pauer, Z. Zhou, S. Dimitriadou, A. Schmidt-Ott, J. Wang, *Environ. Sci.: Nano.* **2024**, *11*, 1023.

Acknowledgements

The authors gratefully acknowledge the Fonds De La Recherche Scientifique – FNRS (10.13039/501100002661) for supporting this work.

Mesoporous Ni/ZrO_2-SiO_2 catalysts for the Dry Reforming of Methane

Luciano Atzori[*,1,2], Daniela Meloni[1], Elisabetta Rombi[1,2], M. Giorgia Cutrufello[1,2]
[1]*University of Cagliari, Department of Chemical and Geological Sciences, Monserrato (CA), Italy.*
[2]*National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence, Italy.*
** luciano.atzori@unica.it*

Significance and Relevance

This work highlights the crucial role of SiO_2 as a promoter for Ni/ZrO_2 catalysts. A relatively low content of silica is able to promote a very high dispersion of nickel species, which is preserved even after calcination up to 850 °C. This aspect is particularly important when the endothermic character of a reaction requires high operating temperatures, as in the case of the Dry Reforming of Methane (DRM), by which carbon dioxide and methane are converted into syngas. Due to the high Ni dispersion, the optimized silica-containing catalysts exhibit very high CO_2 and CH_4 conversions even under severe reaction conditions.

Preferred choice for the topic: CO_2 utilization and recycling
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The ever-increasing exploitation of fossil fuels necessary to meet the growing worldwide energy demand is leading to a series of detrimental environmental effects, related to the emissions of greenhouse gases in the atmosphere. For this reason, the development of technologies aimed at using CO_2 and CH_4 can be considered of primary importance in the area of energy research. Among these technologies, the Dry Reforming of Methane (DRM) process plays a crucial role, since it involves the utilization of both CO_2 and CH_4 as raw materials to produce syngas with a molar ratio close to 1:1.[1]

Although noble metal-based systems are less sensitive to carbon deposition, their high cost makes nickel-based catalysts a viable alternative, since they are relatively active and reasonably inexpensive.[2] Due to its peculiar properties, zirconia can be considered as a suitable support for nickel-based catalysts.[3] In light of this, in the present study, different Ni-Zr based catalysts were prepared, characterized and tested in terms of catalytic performance in the DRM process.

Materials and Methods

Different Ni/ZrO_2 catalysts (Ni content in the range 2-15 wt%), were prepared by reducing their corresponding mixed oxides, synthesized by a coprecipitation procedure assisted by a templating agent (cetyl trimethyl ammonium bromide). In order to investigate the effect of the presence of silica both on the properties of the mixed oxides and on the catalytic performance of the reduced systems, samples with or without SiO_2 (named *x*NiO/ZrO_2-SiO_2 and *x*NiO/ZrO_2, respectively, where *x* represents the nickel content) were prepared. Different portions of the materials were calcined in the range 450-850 °C, then characterized by means of Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES), X-Ray diffraction (XRD), N_2 physisorption, Transmission Electron Microcopy (TEM), Temperature Programmed Reduction (H_2-TPR) and H_2 pulse chemisorption. After reduction with pure hydrogen of the mixed oxides calcined at 850 °C, the catalytic tests were performed at 800 °C and at atmospheric pressure, with a stoichiometric CO_2/CH_4 molar ratio (1:1) and space velocity (*SV*) in the range 60000-240000 $cm^3\ h^{-1}\ g_{cat}^{-1}$.

Results and Discussion

Materials are characterized by type IVa N_2 physisorption isotherms and type H2 hysteresis loops, typical of mesoporous materials. Compared to the Si-free mixed oxides, the xNiO/ZrO_2-SiO_2 materials exhibit higher specific surface areas, with values close to 100 $m^2\ g^{-1}$ even after calcination at 850 °C. In addition, XRD patterns of the samples containing SiO_2 show a lower degree of crystallinity of both zirconium and nickel species, with reflections ascribable to ZrO_2 (tetragonal) and NiO (cubic) which

become clearly visible only after calcination at temperature higher than 650 °C. For all the *x*NiO/ZrO_2-SiO_2 samples calcined at 850 °C, nanocrystallites average sizes of 6 and 7 nm are estimated for ZrO_2 and NiO phases, respectively; on the other hand, in absence of silica nanocrystals sizes more than double are found. By comparing the H_2-TPR profiles of the samples with the same content of Ni, in the Si-containing samples the main reduction peak results to be shifted towards higher temperatures, clearly highlighting the presence of NiO species that interact more strongly with zirconia. Although all the prepared catalysts are found highly active for the DRM reaction, some important differences can be noted between the two series of materials prepared. By comparing the catalytic performance of 10Ni/ZrO_2-SiO_2 and 10Ni/ZrO_2, indeed, higher CO_2 and CH_4 conversions are obtained with the sample containing silica, as a direct consequence of the better dispersion of the Ni species. In addition, the activity of the sample 10Ni/ZrO_2-SiO_2 is found very stable throughout the reaction time (ca. 6 h), showing CO_2 and CH_4 conversions close to 90 mol% and 80 mol%, respectively, even when performing the catalytic test at *SV*= 240000 $cm^3\ h^{-1}\ g_{cat}^{-1}$ (Figure 1).

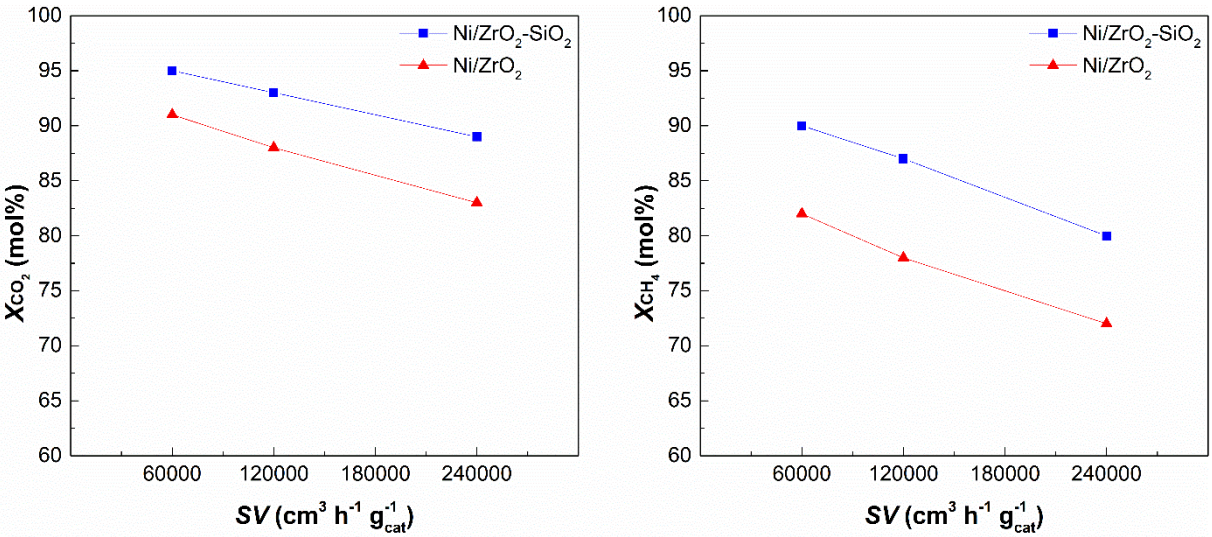


Figure 1. CO_2 and CH_4 conversion values as a function of space velocity (*SV*). Other reaction conditions: atmospheric pressure; T_{reac} = 800 °C; m_{cat} = 0.025 g; CO_2/CH_4 = 1 mol mol^{-1}.

Different Ni/ZrO_2 catalysts were prepared by a coprecipitation procedure assisted by a templating agent. Even after calcination at 850 °C, the Si-containing samples are all characterized by very high specific surface areas and nickel dispersions, especially if compared with the corresponding Si-free materials. As a consequence, the xNi/ZrO_2-SiO_2 catalysts exhibit better catalytic performance, being able to promote very high CO_2 and CH_4 conversions even at very high space velocity.

References

1. Z. Bian, S. Das, M.H. Wai, P. Hongmanorom, S. Kawi, *ChemPhysChem* **2017**, 18, 3117-3134.
2. Y. Cai, Y. Zhang, X. Zhang, Y. Wang, Y. Zhao, G. Li, G. Zhang, *Atmosphere* **2023**, 14, 1323.
3. W. Li, Z. Zhao, F. Ding, X. Guo, G. Wang, *ACS Sustainable Chem. Eng.* **2015**, 3, 3461-3476.

Enhanced Photocatalytic Performance of (TiO_2-WO_3) Supported on $Sr_4Al_{14}O_{25}$:Eu, Dy under Visible Light

Hyun-sung KANG, Jung-Sik KIM*
The University of Seoul, Department of Materials Science and Engineering, Seoul 02504, Republic of Korea
** e-mail corresponding: jskim@uos.ac.kr*

Significance and Relevance

- ✓ TiO_2/WO_3 nano-crystalline was coated on the bead-shaped supporter of $Sr_4Al_{14}O_{25}$:Eu^{2+},Dy^{3+} long-lasting phosphor by a hydrothermal reaction method.
- ✓ The photocatalytic decomposition rate varied significantly with the hydrothermal reaction temperature and ratio of TiO_2 and WO_3.
- ✓ Optimum photocatalytic efficiency for the (TiO_2-WO_3)/phosphor composite was occurred with the 5:5 ratio of TiO_2 to WO_3 and heat treatment temperature of 550 °C.

Preferred and 2nd choice for the topic: (1) Photocatalysis and photoelectrocatalytic approaches, solar energy utilization, and (2) Air cleaning and combustion

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Photocatalytic materials have received increasing attention as materials that can decompose harmful environmental pollutants in an eco-friendly manner through redox reactions using light energy. Among the various photocatalytic materials, TiO_2 is the most widely used because it is chemically stable and has a band gap of 3.2 eV, in which photo excitation reactions can occur efficiently. In this study, TiO_2 and WO_3 have been hybridized and supported on the long-lasting phosphor of $Sr_4Al_{14}O_{25}$:Eu,Dy. In the hybrid photocatalyst of (TiO_2-WO_3)-coated long-lasting phosphor, the phosphor may act as an internal light source toward the acceleration or sustenance of photocatalytic reactivity even in the absence of external light irradiation.

Materials and Methods

The long-lasting phosphor powders of $Sr_4Al_{14}O_{25}$:Eu^{2+},Dy^{3+} was prepared to be bead-shaped supporter, following the coating of TiO_2 and WO_3 nano-particles by a hydrothermal synthesis. For the fabrication of phosphor beads, $Sr_4Al_{14}O_{25}$:Eu^{2+},Dy^{3+} phosphor powders were mixed with Na_2SiO_3 aqueous solution to be slurry state. The phosphor droplets were made by extruding the phosphor slurry through 3 mm nozzle syringe and dropping into a 10 wt.% $CaCl_2$ solution, then separated from the solution and annealed at 350 °C for 3h.

For the fabrication of (TiO_2-WO_3)-coated phosphor beads, TiO_2/WO_3-precursor was prepared by mixing titanium isopropoxide (TTIP), tungsten precursor ($Na_2WO_4 \cdot 2H_2O$), ethanol, deionized water, and HNO_3 with appropriate volume ratios, respectively. Then, the TiO_2/WO_3--sol solution was mixed with the prepared $Sr_4Al_{14}O_{25}$:Eu^{2+},Dy^{3+} phosphor beads, transferred into a Teflon-lined autoclave and heat treated in a dry oven at 150 °C for the selected time of hydrothermal reaction.

The photocatalytic performance of the (TiO_2-WO_3)-coated phosphor beads was analyzed with respect to the photobleaching effect of methylene blue and decomposition of toluene gas by UV/Vis spectrometer and gas chromatography (GC), respectively.

Results and Discussion

A photocatalytic performance was investigated by measuring the decomposition of toluene gas under visible light irradiation in 1 L Teflon gas bag with 10g sample of (TiO_2-WO_3)-coated $Sr_4Al_{14}O_{25}$:Eu^{2+},Dy^{3+} beads. The hydrothermal reaction temperature of (TiO_2-WO_3)-coating process was fixed at 550 °C, while the ratio of TiO_2 to WO_3 was 10:0, 7:3, 5:5, 3:7, and 0:10. For comparison, the

photocatalytic performance of $TiO_2/Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ composite beads without WO_3 was investigated.

Fig. 1 shows the difference in the photocatalytic efficiency based on the ratio of TiO_2 to WO_3 under visible light irradiation. The highest photocatalytic efficiency occurred when the ratio of TiO_2 to WO_3 was 5:5, where the photocatalytic decomposition of toluene reached over 70% after 90 min. The (TiO_2-WO_3)/$Sr_4Al_{14}O_{25}$: Eu^{2+},Dy^{3+} beads with 7:3 of TiO_2 to WO_3 decomposed 65% of toluene gas after 90 min, whereas that of 3:7 of TiO_2 to WO_3 decomposed 50% of toluene gas. Meanwhile, the $TiO_2/Sr_4Al_{14}O_{25}$: Eu^{2+},Dy^{3+} beads without WO_3 showed 40% decomposition rate of toluene, indicating significantly low photocatalytic efficiency, compared with other samples with WO_3.

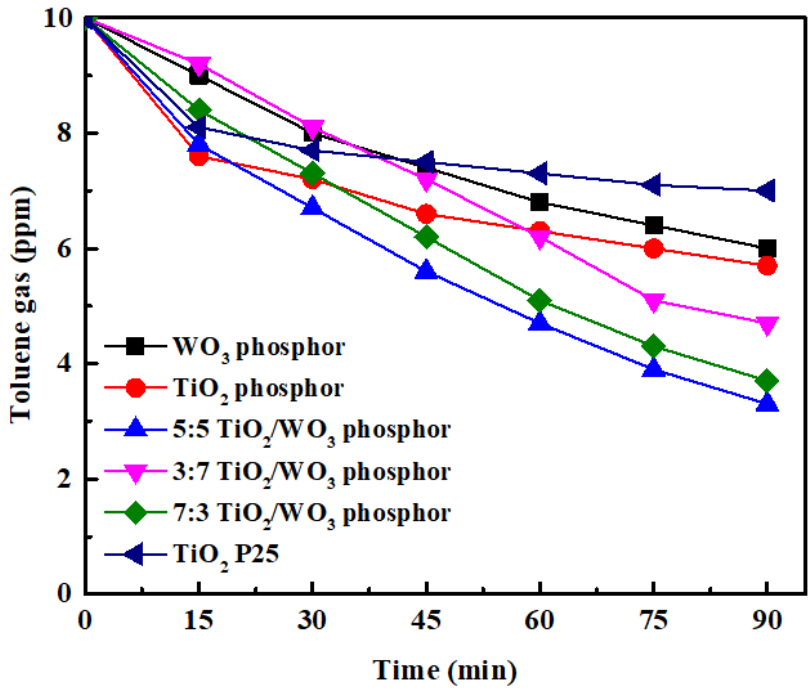


Figure 1. Variations of toluene decomposition under visible light illumination for (TiO_2-WO_3)/phosphor composites.

References

1. A. Mishra, A. Mehta, S. Basu, J. Environ. Chem. Eng. **2018**, 6, 6088; Q. Guo, C. Zhou, Z. Ma, X. Yang, Adv. Mater. **2019**, 31, 1
2. S. Mavengere, J.-S. Kim, Mater. Sci. Semicon. Proc. **2023**,153, 107132
3. H. Yang, B. Yang, W. Chen, J. Yang, Catalysts **2022**, 12, 1263
4. W. Koe, J. Lee, W. Chong, Y. Pang, L. Sim, Environ. Sci. Pollut. Res. **2020**, 27, 2522

Acknowledgements

This study was supported by the 2024 Research Fund of the University of Seoul.

Ni nanoparticles decorated over Y^{3+} promoted CeO_2 single-atom catalysts for enhanced low-temperature CO_2 methanation

Neha CHOUDHARY[1], Navdeep SRIVASTAVA[2], Biplab GHOSH[3], Patrick DA COSTA[*1]

[1]*Institut Jean Le Rond D'Alembert, Sorbonne Université, CNRS UMR 7190, 2 Place de la Gare de Ceinture, 78210 Saint-Cyr-L'Ecole, France*
[2]*Department of Chemistry, Indian Institute of Technology-Indore, Simrol, Khandwa Road, 433552, India*
[3]*BARC Beamlines Section, Indus-2, RRCAT, Indore, 452013 India*
*patrick.da_costa@upmc.fr

Significance and Relevance

In this work, Ni nanoparticles decorated over Y^{3+} doped over CeO_2 support Single-atom catalysts were prepared to enhance the catalytic activity and selectivity of typical Ni/CeO_2 catalysts. The XPS spectra confirm that the doping of Y^{3+} increases the oxygen vacancies over CeO_2 and consequently enhances the catalytic activity at low reaction temperatures. For comparison, impregnated NiY/CeO_2 and Ni/CeO_2 catalysts were also tested for methanation, which showed less selectivity towards methane products. Moreover, STEM-EDS analysis confirmed the uniform dispersion of Yttrium over CeO_2 in synthesized SACs. The results demonstrate the synergistic effect of Ni with Y to enhance the active sites over CeO_2 support for enhanced catalytic performance.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling, Sustainable and clean energy production and transport
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster) **Oral preferred** or short oral

Introduction and Motivations

The hydrogenation of CO_2 into CH_4 is an efficient approach for addressing environmental issues related to CO_2.[1] The methanation of CO_2 is receiving increasing focus because of its growing relevance in applications like the power-to-gas concept and long-duration space exploration missions. In this context, catalysts play a crucial role in improving the selectivity towards methane, particularly at low reaction temperatures, and for this purpose, Ni-based catalysts are proven to be good catalysts owing to their low cost. However, Ni/CeO_2 has been extensively explored for the methanation reaction owing to the synergistic effect between Ni and CeO_2 support due to its high surface area and great oxygen mobility. Recently, Cr^{3+} and Eu^{3+} doping over Ni/CeO_2 was reported to generate surface oxygen vacancy over ceria support by creating more $Ce^{3+,}$ consequently enhancing the catalytic performance.[2,3] Moreover, Zhang et al.[4] the dual-active-site SACs were explored where Ru SACs over CeO_2 were prepared with Ni nanoparticles boosted catalytic performance for CO_2 methanation. SACs have high exposure to active sites and enhanced shows both properties of homogeneous and heterogeneous catalysts.[5] On the other hand, the effect of Y over Ni-based catalysts for CO_2 methanation was well-explored by our group, where Yttrium improved the basicity of catalysts and led to stabilizing the catalyst for carbon formation.[6,7] Hence, keeping this in mind, we synthesized Y/CeO_2 SACs with ~5 wt% of Y loading and then Ni nanoparticles were impregnated over as synthesized SACs and named as NiY/CeO_2. Furthermore, for comparison, impregnated NiY NPs over CeO_2 and Ni/CeO_2 were also prepared and tested for methanation reaction. All these catalysts are well-characterized and analyzed for CO_2 methanation reaction.

Results and Discussion

Y/CeO_2 SACs with 1:9 molar ratio was synthesized via co-precipitation method and further Ni nanoparticles were impregnated over as prepared Y/CeO_2 SACs via incipient wetness impregnation method. For comparison, Ni and Y together impregnated over ceria support were prepared by the impregnation method and named as Ni/CeO_2-imp. Additionally, Ni/CeO_2-imp was also prepared without using Yttrium salt. These prepared catalysts were characterized via various characterizing

techniques like PXRD, H_2-TPR, CO_2-TPD, H_2-TPD, BET, HR-TEM, STEM-EDS, XPS, EXAFS, ICP-OES etc. PXRD analysis of fresh catalysts confirmed the doping of Y over ceria while shifting of (111) plane of ceria was observed to higher 2θ value, which may be because of the change in interplanar spacing in ceria lattice after doping of Y^{3+} in case of NiY/CeO_2 SACs. Furthermore, the presence of NiO was confirmed through PXRD matches with JCPDS#96-900-8694. N_2 adsorption-desorption analysis confirmed the high surface area and CO_2 TPD showed high basicity in comparison to Ni/CeO_2 catalyst. Furthermore, STEM-EDS analysis was performed, which showed uniform dispersion of Y over ceria even after impregnation of Ni NPs. ICP-OES analysis is in good agreement with the wt% obtained via STEM-EDS analysis where Y is ~5 wt% and Ni is ~7 wt% observed over ceria support. XPS analysis confirmed that NiY/CeO_2 SACs have more surface oxygen vacancies than Ni/CeO_2-imp catalysts, confirming the effect of Y doping over ceria support. Also, XPS spectra revealed higher Ce^{3+} in the case of NiY/CeO_2 than Ni/CeO_2 catalysts. After careful characterization, the set of all catalysts was utilized for the CO_2 methanation reaction, where NiY/CeO_2 showed superior catalytic activity with 82% conversion and ~100% selectivity over undoped Ni/CeO_2-imp and NiY/CeO_2-imp catalysts at 350℃ (**Figure 1**). Moreover, a long test run was also performed to utilize the robustness of the NiY/CeO_2 SAC for 40 hours, which showed no significant change in catalytic performance. These results provide a valuable perspective for assessing the hydrogenation process, thereby establishing a link between structure and activity performance. Additionally, the results offer important insights into the role of oxygen vacancies and their impact on catalytic activity.[6]

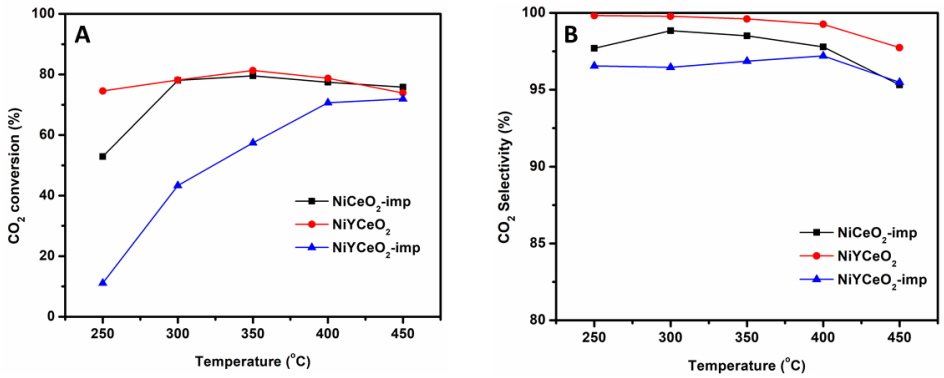


Figure 1. Methanation results of CO_2 methanation with NiY/CeO_2 catalysts (A) conversion and (B) selectivity.

References

[1] N. Choudhary, K. Nabeela, N. Mate, S. M. Mobin, *RSC Sustain.* **2024**, DOI 10.1039/D4SU00069B.
[2] Z. Zhang, Z. Yu, K. Feng, B. Yan, *Appl. Catal. B Environ.* **2022**, *317*, 121800.
[3] X. Xu, L. Liu, Y. Tong, X. Fang, J. Xu, D. Jiang, X. Wang, *ACS Catal.* **2021**, *11*, 5762–5775.
[4] T. Zhang, P. Zheng, F. Gu, W. Xu, W. Chen, T. Zhu, Y.-F. Han, G. Xu, Z. Zhong, F. Su, *Appl. Catal. B Environ.* **2023**, *323*, 122190.
[5] N. Choudhary, S. Jiang, H. Pham, G. Kedarnath, A. Datye, J. T. Miller, A. K. Tyagi, M. M. Shaikh, *Appl. Catal. B Environ.* **2024**, *344*, 123627.
[6] C. Sun, P. Beaunier, V. La Parola, L. F. Liotta, P. Da Costa, *ACS Appl. Nano Mater.* **2020**, *3*, 12355–12368.
[7] C. Sun, K. Świrk Da Costa, D. Wierzbicki, M. Motak, T. Grzybek, P. Da Costa, *Int. J. Hydrog. Energy* **2021**, *46*, 12169–12179.

Acknowledgments

We thank the PEPR Power CO_2, Sorbonne University and CNRS for financial support. We would like to acknowledge the Instrumentation facility of Sorbonne University for STEM, University of Lille for PXRD, IC2MP for ICP-OES, MNIT-Jaipur, India for XPS and synchrotron facility at RRCAT, India for EXAFS analysis.

Novel bimetallic La-Ni and Ba-Ni ceramic foams for dry reforming of methane

María CÓRDOBA[*1], Andoni CHOYA[1], Beatriz DE RIVAS[1], Jose Ignacio GUTIÉRREZ-ORTIZ[1], Rubén LÓPEZ-FONSECA[1]
[1]*Technologies for Environmental Sustainability Group, Department of Chemical Engineering, Faculty of Science and Technology, University of The Basque Country UPV/EHU, Barrio Sarriena s/n, Leioa, Bizkaia E-48940, Spain.*
**maria.cordoba@ehu.eus*

Significance and Relevance

Dry reforming of methane (DRM) represents a technology for the valorization of CO_2 and the decarbonization of industrial processes. The resulting syngas that is widely utilized in Fischer-Tropsch synthesis and ammonia production, among others. The most active catalyst for this reaction is Ni supported on alumina. The implementation of DRM requires the use of structured catalysts capable of processing large flow rates of CH_4 and CO_2. Furthermore, the design of active and stable nickel catalysts with a high resistance to coke formation and sintering of the active particles is essential.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling; H_2 storage and transportation, green H_2 production, hydrogen vectors.
Preferred presentation: Oral preferred or short oral

Introduction and Motivations

Climate change represents a significant challenge for contemporary society, prompting governments and institutions to pursue the decarbonization of energy sources[1]. An alternative solution is the valorization of CO_2 and CH_4 through DRM which generates syngas, one of the main intermediate products[2]. This process typically operates at elevated temperatures between 650 and 850 °C and high flowrates in the presence of a Ni-based catalyst[3]. This demands the use of structural catalysts with lower pressure drop, as well as efficiently performs in terms of resistance to deactivation by coking and sintering. However, under these conditions, catalysts frequently undergo deactivation due to the formation of coke and sintering of active metal crystallites[4]. To mitigate coke formation, the addition of a ceramic foam as a support and a second metal which promotes its gasification, such as lanthanum or barium. Lanthanum is known for its coke-gasification property and barium for its basicity. Adding these to the bare catalyst can improve its stability. This study proposes a characterization and performance evaluation of the two promoters in DRM.

Materials and Methods

Modified $NiAl_2O_4$ precursors with a promoter/Ni molar ratio of 0.06 and Ni/Al molar ratio of 0.5 were synthesized by Solution Combustion Synthesis (SCS) from a $Ni(NO_3)_2$, $Al(NO_3)_3$, and $La(NO_3)_3$ or $Ba(NO_3)_2$ solution and glycine as fuel. The open-cell foam was dipped into this gel several times with an intermediate calcination step at 300 °C until a 10wt% loading was achieved. The resulting structured ceramic foam was stabilized at 850 °C for 4 h. The physico-chemical characterization of the samples was carried out using N_2 physisorption, XRD, H_2-TPR and CO_2-TPD. Catalytic performance was assessed at 700 °C, and a space velocity of 96,000 h^{-1} using a 10%CH_4/10%CO_2/80%N_2 feed stream for 72 h at a total flow rate of 800 cm^3 min^{-1}. Prior to the reaction, the ceramic foams were reduced at 850 °C for 2 h with a 5%H_2/N_2 gas stream. The used catalysts were characterized via DTG.

Results and Discussion

X-ray diffractograms of the calcined foams revealed the presence of signals indicative of $NiAl_2O_4$ spinel, as well as mullite, cordierite and cristobalite, which can be attributed to the constitutional oxides of the foam substrate. No promoters were identified due to their low concentration and high dispersion. The crystallite size of the $NiAl_2O_4$ phase was estimated using the Scherrer equation, obtaining 22 nm

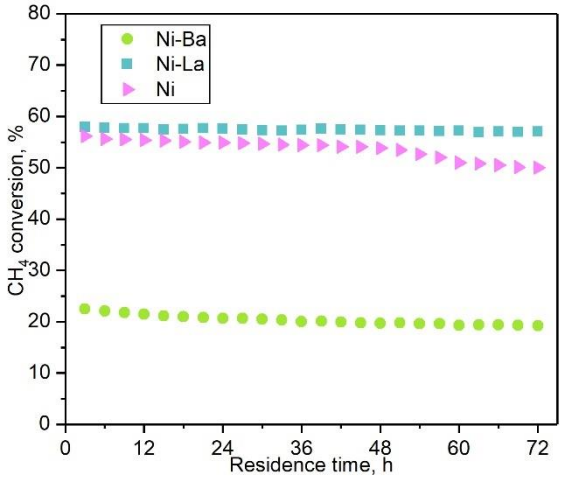


Figure 1. Catalytic performance of the lanthanum, barium and non-promoted catalysts.

and 30 nm for Ni-La and Ni-Ba precursors, respectively. Reduced catalysts have been characterized via N_2 physisorption presenting a BET area of 4.8 and 2 m^2 g^{-1} for the Ni-La and Ni-Ba samples, respectively. This low area is due to the BET area of the ceramic foam, which is only 0.2 m^2 g^{-1}, and the catalyst constitutes only 10% of the total mass. DRX analysis also revealed the crystallite size following reduction, which was 9 nm for the La foam and 12 nm for the Ni-Ba counterpart. No $NiAl_2O_4$ was identified, validating the reduction method employed for the ceramic foams. H_2-TPR analysis revealed two distinct reduction events: one for temperatures below 600 °C for segregated NiO and other above 600 °C for $NiAl_2O_4$ spinel reduction. The integration and quantification of the reduction profiles demonstrated that over 88% of the nickel incorporated in the Ni-La foam was in the form of $NiAl_2O_4$, whereas this fraction in the Ni-Ba sample was only 67%. This evidences that barium prevents the reaction between nickel and alumina, while lanthanum limits the formation of the undesired NiO. CO_2-TPD was conducted to estimate the basic sites of the reduced foams, thereby obtaining the total basicity of the foams and their classification as weak (0-200 °C), medium (200-500 °C) or strong (> 400 °C) basicity. The Ni-La foam exhibited a total basicity of 0.06 mmol CO_2 g^{-1} and displayed 86% of strong basicity, whereas the Ni-Ba foam presented a higher total basicity (0.14 mmol CO_2 g^{-1}) with a 91% of strong basicity.

The catalytic performance was evaluated in terms of CH_4 and CO_2 conversions and H_2/CO ratio and compared with the non-promoted ceramic foam with Ni/Al molar ratio of 0.5. Ni-La sample obtained a high conversion, reaching approximately 60%, and exhibited a remarkable stability. In contrast, the bare NiAl foam achieved a similar conversion but began to show signs of deactivation after 48 h. This behavior was assigned to a better coke-gasification properties and a smaller crystallite size for the active phase in Ni-La catalyst. The Ba-promoted catalyst displayed a comparatively lower conversion rate, potentially due to the low nickel spinel formation, yet it demonstrated a more stable conversion than the NiAl foam. The H_2/CO ratio showed a different tendency as the conversion, with 1.5, 1.2 and 1 molar ratios for the Ba, La and NiAl catalysts, respectively.

Lastly, coke formation was evaluated via TGA resulting in 0.02, 0.106 and 0.77 mg_{coke} mg_{foam}^{-1} for the Ni-La, Ni-Ba and NiAl foams, respectively. This indicates a reduction in coke formation in the promoted catalysts and, thereby enhancing their stability.

References

1. A. Choya, B. de Rivas, M.L. No, J.I. Gutiérrez-Ortiz, R. López-Fonseca, *Fuel* **2024**, 130166, 350.
2. J.J. Bolívar-Caballero, I. Nuran-Zaini, W. Yang, *Applications in Energy and Combustion Science,* **2022**, 100064, 10.
3. C. Wang, Y. Wang, M. Chen, D. Liang, Z. Yang, W. Cheng, Z. Tang, J. Wang, H. Zhang, *International Journal of Hydrogen Energy* **2021**, 5852-5874, 46.
4. A. Abdulrasheed, A.A. Jalil, Y. Gambo, M. Ibrahim, H.U. Hambali, M.Y.S. Hamid, *Renewable and Sustainable Energy Reviews* **2019**, 175-193, 108.

Acknowledgements

This research was funded by the Ministry of Science and Innovation (PID2022-141583OB-I00), Basque Government (IT509-22) and the University of The Basque Country UPV/EHU (DOCREC21/23). The author wishes to thank the technical and human support provided by SGIker (UPV/EHU).

Design of nanostructured Cu oxides for the electrocatalytic CO_2 reduction

Falak SHAFIQ*,[1] Davide MELOTTO[1], Tatiana RODRIGUEZ-FLORES[1], Laura VIGNI[2], Mariangela LONGHI[2], Marco MONTALBANO[2], Maria Vittoria DOZZI[2], Lorenzo MINO[3], Roberto NISTICO'[1]
[1]*University of Milano-Bicocca, Dept. of Materials Science, Via R. Cozzi 55, Milano, Italy.*
[2]*University of Milano, Dept. of Chemistry, Via C. Golgi 19, Milano, Italy.*
[3]*University of Torino, Dept. of Chemistry and NIS Centre, Via P. Giuria 7, Torino, Italy.*
** f.shafiq@campus.unimib.it*

Significance and Relevance

In the present study, Cu oxides-based materials, selected for their strong coordination ability with CO intermediates, were synthesized following different soft-chemistry approaches, varying the final morphology (*i.e.*, size/shape, aspect ratio, crystal planes orientation). After performing morphological (SEM), and structural (XRD) characterizations, such materials were thus tested in the electrocatalytic CO_2 reduction (e-CO_2R), showing a different selectivity toward specific C_1-C_{2+} products depending on the final morphology.

Preferred and 2nd choice for the topic:

- CO_2 utilization and recycling.
- Fundamental advances in understanding catalysis.

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The current energetic paradigm is based on the consumption of fossil fuels to produce energy. However, the extensive use of traditional fossil fuels is one of the major causes of the release of greenhouse gases (*e.g.*, CO_2) in the atmosphere with consequent threat to the global climate balance and depletion of fossil fuels resources. Among the different alternative solution, electrochemistry is a very promising and appealing technology potentially able to accomplish the conversion of renewable sources into fuels for energy applications in a green way, alternative to the traditional fossil fuels, such as the CO_2 reduction (CO_2R) into valuable C_1-C_{2+} products. However, the possibility of exploiting these catalytic routes to produce fuels at large scale is still strongly affected by the selection of the best catalysts and the optimization of the process parameters.[1,2]

Materials and Methods

CuO systems were synthesized applying either a hydrothermal (H1) or a co-precipitation route (P2). Route H1: CuO formation occurred by using an alkaline solution of 6 M NaOH as precipitating agent. The synthesis took place in an autoclave by varying the treatment temperature between 150 °C and 200 °C, in a time interval of 10 hours. Route P2: synthesis took place at constant temperature (80 °C), by varying both the concentration of the precipitating agent NaOH (*i.e.*, 0.50 M, 0.75 M, 1.00 M, and 2.00 M), and the reaction time (either 30 minutes, or 2 hours).

Cu_2O systems were synthesized following a selected protocol involving the precipitation of Cu_2O in presence of PEG, L-ascorbic acid as reducing agent, and NaOH as precipitating agent.[3] Different parameters (*e.g.*, stirring time, temperature, amount of reducing agent) were systematically optimized.

Results and Discussion

The following three main CuO catalysts were investigated in the e-CO_2R: *i)* H1-01 synthesized by the hydrothermal route and exhibiting a large (0.8-1.5 µm) prismatic-tabular morphology (Fig. 1A), *ii)* P2-02 synthesized by the precipitation route with a small (< 500 nm) sheet-like morphology (Fig. 1B) and *iii)* P2-04 synthesized by means of the precipitation route with large (0.8-1.2 µm) sheet-like morphology (Fig. 1C). Electrocatalytic tests, performed in a dedicated flow cell set-up, confirmed that the products selectivity strongly depended on both morphology and dimensions of the CuO catalysts.

In particular, at low applied current density (50-100 mA cm^{-2}), H1-01 favors the CO_2-to-CO conversion, whereas at high current density this system becomes more unstable and less selective. Differently, at low current density, both P2-02 and P2-04 systems favor the CO_2-to-C_2H_4 conversion, whereas at high current density, the selectivity toward the detrimental hydrogen evolution reaction (HER) starts becoming predominant. Only the P2-04 shows an increased CO_2-to-CH_4 conversion selectivity.

High resolution TEM analysis and FTIR spectroscopy tests in presence of probe molecules are ongoing to clarify the role played by the morphology in term of catalytic selectivity.

The performances attained with the following three main Cu_2O-based samples in the e-CO_2R is currently ongoing: *i)* F1-03 composed of small quasi spherical Cu_2O NPs with the presence of large polyhedral metallic Cu nanoparticles (NPs), *ii)* F1-07 made by small quasi spherical pure Cu_2O NPs, and *iii)* F1-12 composed of large polyhedral metallic Cu NPs (for the sake of comparison).

The obtained results will provide an effective screening of the fundamental properties necessary for maximizing the catalytic performances and specific selectivity of these systems in the e-CO_2R.

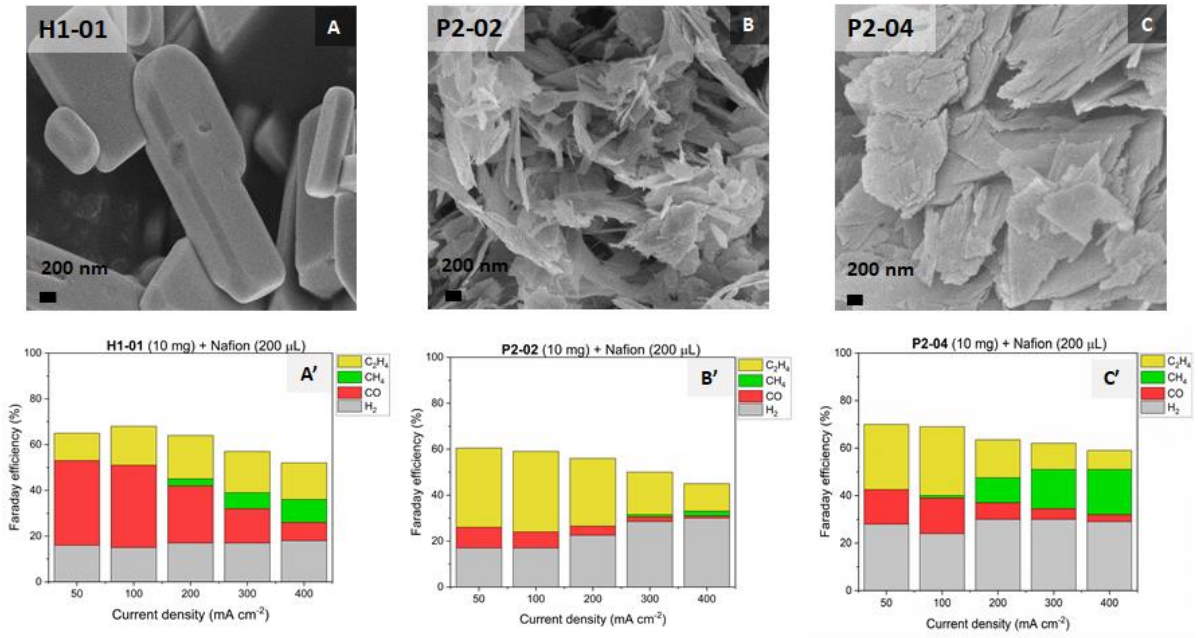


Figure 1 SEM micrographs (top) and Faradaic Efficiencies attained in the e-CO_2R test (bottom) of H1-01 (A, A'), P2-02 (B, B') and P2-04 (C, C') CuO-based materials.

References

1. A.R. Woldu, Z. Huang, P. Zhao, L. Hu, D. Astruc, *Coord. Chem. Rev*. **2022**, *454*, 214340.
2. R.-Z. Zhang, B.-Y. Wu, Q. Li, L.-L. Lu, W. Shi, P. Cheng, *Coord. Chem. Rev*. **2020**, *422*, 213436.
3. M. Mallik, S. Monia, M. Gupta, A, Ghosh, M.P. Toppo, H. Roy, *J. Alloys Compd*. **2020**, *829*, 154623.

Acknowledgements

This work received financial support from MUR (Italy) and the European Union – Next Generation EU, Mission 4, Component 1, CUP (H53D23008000001) through the PRIN Project PERFECT (N. P2022TK9B9) and CUP (H53D23004490001) through the PRIN Project MAPEC (N. 2022599NR3).

Unravelling S Poisoning Effects on Ru/Al_2O_3 CO_2 Methanation Catalysts Through *in-situ* and *ex-situ* Approaches

Clara LARGHI[1], Alessandro PORTA[1], Carlo Giorgio VISCONTI[1], János SZANYI[2]*, Luca LIETTI[1]*
[1] *Dipartimento di Energia, Politecnico Di Milano, Milano, 20156, Italy*
[2] *Institute for Integrated Catalysis, Pacific Northwest National Laboratory, Richland, 99352, WA, USA*
**janos.szanyi@pnnl.gov; luca.lietti@polimi.it*

Significance and Relevance

Sulfur contaminants in CO_2 flows strongly hinder the methanation process. This study used *ex-situ* and *in-situ* poisoning to analyze sulfur's impact on the morphology and activity of a 4% Ru/Al_2O_3 catalyst. Additionally, a kinetic model was developed able to effectively describe the catalyst's deactivation.

Preferred choice for the topic: CO_2 utilization and recycling
Preferred presentation: Oral preferred

Introduction and Motivations

The constant increase of the average temperature on Earth due to greenhouse gases emissions is nowadays leading to a revolution in the energy sector. In this context, CO_2 hydrogenation to Synthetic Natural Gas (SNG) has already been proved to be a viable solution for both renewable energy storage and CO_2 emission reduction, two of the main challenges of energy transition [1]. However, when dealing with CO_2 streams, the presence of contaminants must be taken into account. Among these, sulfur-containing compounds are present in biogenic as well as in fossil-sourced CO_2, and their presence is detrimental to catalytic methanation processes [2,3]. In this study, various *ex-situ* and *in-situ* techniques are employed to elucidate the impact of sulfur on the characteristics and catalytic behavior during CO_2 hydrogenation to methane over a 4% Ru/Al_2O_3 catalyst. Additionally, the observed effects were rationalized with a suitable kinetic model as a function of the sulfur content.

Materials and Methods

The Ru-based catalyst is prepared by impregnating γ-Al_2O_3 pellets (d_p = 100 µm, Sasol Puralox) with an aqueous solution of $Ru(NO)(NO_3)_3$ salt (Alfa Aesar, Ru 31.5 wt.%). The precursor salt was then decomposed in H_2 flow at 400 °C. *Ex-situ* sulfur poisoning is performed by impregnating in inert environment a reduced 4% Ru/Al_2O_3 catalyst with a solution of $(NH_4)_2S$ diluted in ethanol. The preparation procedure was repeated to obtain samples with different sulfur loadings, ranging from 0.7 – 5.5 mg_S/g_{cat}. The *in-situ* deactivation was carried out over the same 4% Ru/Al_2O_3 catalyst by step feeding 10 ppm of H_2S or COS together with the reactant mixture (H_2/CO_2 = 4 mol/mol) at 310°C and constant GHSV.

The activity analysis was performed after reduction at 400°C under H_2 flow, in a temperature range of 230 - 410°C and at pressure values spanning from 0 to 20 barg. The S effect was studied via H_2 and CO pulse chemisorption, H_2-TPR, TEM and *in-situ* XPS analysis. Moreover, *in-situ* DRIFTS experiments were performed to follow the evolution of the surface species as the S loading was varied.

Results and Discussion

CO_2 reduction the tests on the *in-situ* poisoned catalysts showed a gradual decrease in CO_2 conversion and an increase in CO selectivity with increasing S content (Figure 1A). These results also revealed that the activity on the *ex-situ* and *in-situ* poisoned catalysts showed the same trends, regardless of whether H_2S or COS was fed into the system (Figure 1A).

The conversion values collected on *ex-situ* poisoned samples in the temperature range of 230-410°C and at 0-20 barg, were described with a kinetic model accounting for the S-deactivation. Figure 1B

represents the parity plot of such model, demonstrating its capability to accurately describe the catalyst behavior in the presence of S in different amounts. *In-situ* XPS measurements indicated the presence of Ru sulfides in reducing environment, and as a result the H_2 chemisorption experiments showed a linearly decreasing trend of the amount of H_2 adsorbed as the sulfur content increased. However, the CO adsorption, performed in DRIFTS experiments at room temperature, showed no major differences between the spectra of the poisoned and the clean samples. Instead, the TPD analysis demonstrated that the presence of sulfur weakens the Ru-CO bond, leading to lowering of the desorption temperature of CO (Figure 2). The *operando* DRIFTS setup was also used to study the effect of S on the surface species under reaction conditions. The results pointed out that the formation of formates and bicarbonates were not significantly hindered by the presence of S. At variance, the carbonyls formation shifted to higher temperatures upon increasing the S content. This trend may be attributed to the reduced ability of the poisoned catalysts to activate hydrogen, therefore hampering the reduction of CO_2 to CO.

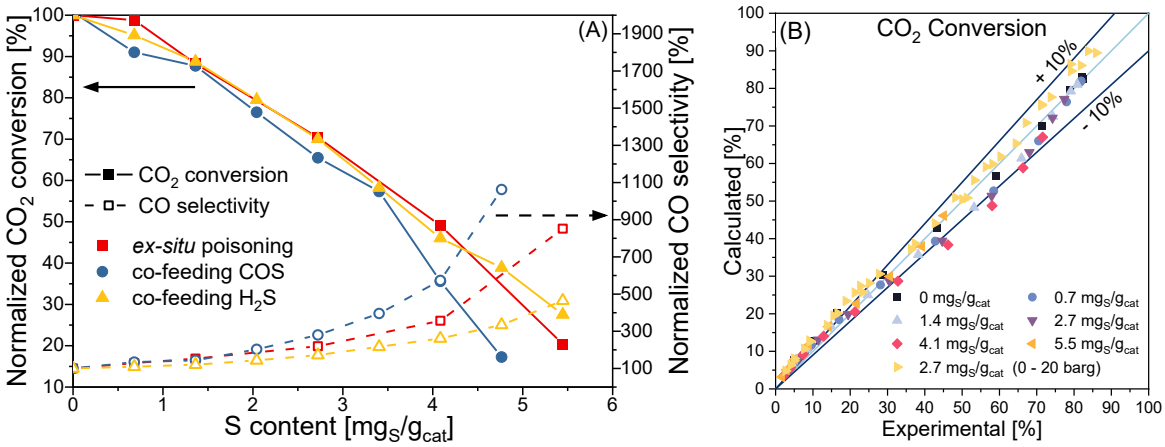


Figure 1. (A) Normalized CO_2 conversion and CO selectivity (100% at 0 mg_S/g_{cat}) trends in function of sulfur content deposited by *ex-situ* and *in-situ* (feeding COS and H_2S) poisoning. T = 310°C; P = 0 barg; H_2/CO_2 = 4 mol/mol. (B) Parity plot of CO_2 conversion kinetic modeling during catalyst deactivation.

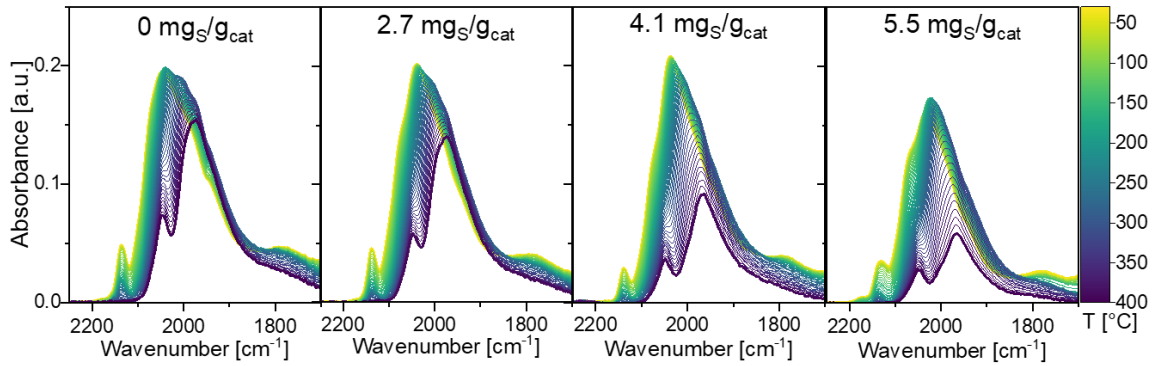


Figure 2. DRIFTS spectra collected during CO-TPD in He over the *ex-situ* poisoned Ru/Al_2O_3 samples.

References

1. C. Vogt, M. Monai, G.J. Kramer, B.M. Weckhuysen, Nat. Catal. **2**, 188–197 (2019).
2. S. Calbry-Muzyka and T. J. Schildhauer, Front. Energy Res. **8**, 570887 (2020).
3. M. Chen, L. Liu, X. Chen et al., Nat. Comm. **15**, 9478 (2024).

Low-critical elements perovskite oxides for clean energy production and CO_2 conversion

Chiara Aliotta*[1], Francesca Deganello[1], Valeria La Parola[1], Laura Valentino[1],
Eleonora La Greca[1] and Leonarda Francesca Liotta[1]
[1] *CNR, ISMN, Via Ugo La Malfa 153, 90146-Palermo, Italy*
** e-mail chiara.aliotta@cnr.it*

Significance and Relevance

To make Solid Oxide Cells (SOCs) competitive for a sustainable future, satisfactory electrocatalysts for oxygen reduction reaction, ORR, and/or for CO_2 reduction reaction CO_2RR, and sustainable materials and processes, are required at the same time. This work concerns the optimization, through doping and synthesis strategies, of the properties of ABO_3 perovskite oxides, the most promising class of SOCs electrocatalysts for clean energy production and CO_2 conversion. The aim is to decrease the critical elements content and to increase the materials performance, by exploiting the knowledge on synthesis-structure-properties relationships.

Preferred and 2nd choice for the topic: Sustainable and clean energy production and transport and CO2 utilization and recycling
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Clean energy transition entails CO_2 utilization and recycling as energy vectors and/or chemicals. Solid oxide cells (SOCs) offer the possibility of producing green energy, working as solid oxide fuel cell (SOFC), and/or to convert CO_2 into valuable fuels, operating as solid oxide electrolysis cell (SOEC). For SOCs, a key technological issue is the development of performing electrocatalysts with structural chemical/thermal stability, peculiar surface and redox properties, good ionic-electronic conductivity and electrocatalytic features towards ORR and/or CO_2RR[1]. Furthermore, a sustainable technology moves together with sustainable materials first in terms of critical element content[2]. Perovskite oxides seem to meet all these requirements, if appropriately doped in A-, B-, or O- sites and tailored by synthesis procedures[3]. Doped-La(Sr)FeO_3 represent a versatile class of perovskites with a good balance between stability/activity/conductivity. It is expected that the replacement of critical Sr with not critical[2] La, Sm or Ce mainly affects mixed ionic-electronic conductivity, whereas electrocatalytic performance is primarily determined by B-site elements as Fe and Al, for ORR, and Fe, Co, Ni and Cu, for CO_2RR. In this work, A- and B-sites co-doping and the less known O-site doping were explored, by selecting compositions with low-content of critical elements. In details, Ce/Sm/Y/Al-doped $SrFeO_3$ were explored for ORR, whereas Cu/Ni/F-doped $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ were studied for CO_2RR. The fine-tuning of their chemical-physical properties was also attained through the synthesis procedures, using solution combustion synthesis or citrate assisted method[4].

Materials and Methods

Herein two class of perovskite oxides are presented for ORR and CO_2RR, respectively. As electrocatalysts for ORR $SrFeO_3$ doped in A-site with Sm, Ce or Y and in B-site with Al were studied. For CO_2RR three different doping strategies were explored for $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$: i) doping the B-site with Cu or Ni ii) fluorine-doping in O-site and iii) co-doping B- and O-sites with Cu/Ni and F. Solution combustion synthesis (SCS) and citrate-assisted method were employed as effective synthesis methodologies in producing perovskite oxides. Structural, surface, textural and redox properties were investigated by X-ray diffraction (XRD) with Rietveld analysis, X-Ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA) and temperature programmed reduction (TPR) in controlled

atmospheres. Electrochemical tests were performed on symmetrical cells by electrochemical impedance spectroscopy (EIS).

Results and Discussion

Figure 1A displays an example of graphical Rietveld fitting of XRD data. X-ray diffraction associated with Rietveld analysis evidenced the incorporation of dopants in the rhombohedral perovskite crystal structures for all studied compositions. H_2-temperature programmed reduction profiles showed that this class of materials exhibits reduction properties and oxygen mobility in the SOCs working temperature range. A satisfactory oxygen vacancies distribution is crucial for oxygen adsorption and oxygen ion drift along the electrocatalyst. Therefore, XPS and TGA experiments were carried out for the evaluation of the suprafacial oxygen vacancies and as well of the bulk oxygen mobility at high temperature (above 400 °C). Figure 1B depicts, for differently doped-$SrFeO_3$, the results relative to TPD step under N_2 flow, carried out during TGA after air treatment. The Sm-doped sample seems to release the highest amount of gaseous O_2, corresponding to the highest weight loss, suggesting that this sample may have the highest amount of oxygen vacancies and bulk oxygen mobility. CO_2-chemisorption properties of doped-$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ evaluated by CO_2-thermogravimetric analysis evidenced a positive effect of copper and fluorine doping (Figure 1C). Structural, redox and surface results were correlated with those obtained by electrochemical impedance spectroscopy in air for doped $SrFeO_3$ and in CO_2 for doped- $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ on symmetrical cells configuration with $Ce_{0.8}Sm_{0.2}O_2$ as electrolyte.

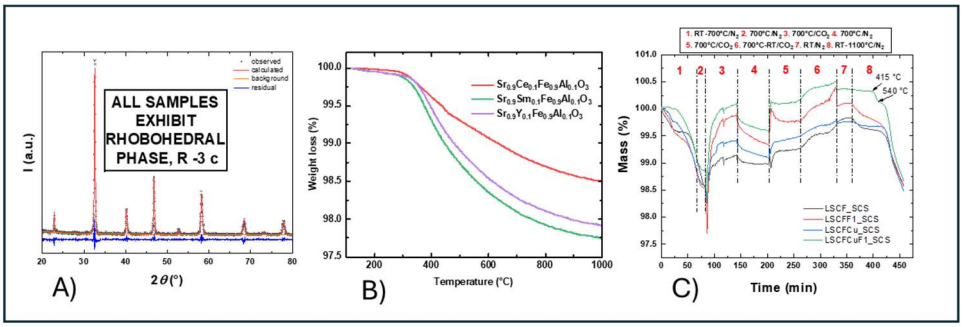


Figure 1. A) Rietveld analysis of XRD data; B) TPD-step of a TGA experiment in air; C) CO_2-TGA experiment consisting of CO_2 chemisorption at 700 °C (2 cycles) and subsequent TPD step.

References

1.M.B. Mogensen, F. Mondi, G. Mogensen, *High-temperature electrolysis-general overview IOP Publishing Ltd* **2023**.

2. https://www.euchems.eu/euchems-periodic-table/

3.W. Li, J. Sunarso, Y. Yang, Y. Chen, C. Ge, W. Wang, Y. Guo, R. Ran, W. Zhou *Energy Reviews* **2024**, 3, 100085.

4. C. Aliotta, M. Costa, L.F. Liotta, V. La Parola, G. Magnacca, F. Deganello, *Molecules* **2023,** 28, 1621.

Acknowledgements

Authors acknowledge the MUR for funding the projects: *MISSION INNOVATION POA 2021-2023 (CUP B82C21001820001), AdP ENEA-CNR (CUP B93C22000630006),* PRIN2022PNRR project OxCellenT (CUP B53D23027440001).

Ni-La Perovskite Catalysts for CO_2 Methanation: Uncovering the Structure-Function Correlation

Luca CONSENTINO[*,1,2], Miriam GONZÁLEZ-CASTAÑO[3], Luis F. BOBADILLA[3], Michelangelo GRUTTADAURIA[2], Leonarda Francesca LIOTTA[1], José Antonio ODRIOZOLA[3]

[1] *ISMN-CNR, Via U. La Malfa 153, 900146 Palermo, Italy*

[2] *STEBICEF Department Ed. 17, University of Palermo, Viale delle Scienze, 90128 Palermo, Italy*

[3] *Department of Inorganic Chemistry, University of Seville (ICMS-CSIC), C/Americo Vespucio 49, 41092 Seville, Spain*

** lucaconsentino@cnr.it*

Significance and Relevance

This work explores Ni-La perovskite catalysts for CO_2 methanation, emphasizing the critical role of catalyst structure and pre-reduction temperature in enhancing conversion efficiency. By comparing one-pot-synthesized lanthanum nickelate with Ni-impregnated lanthanum oxide, it reveals how advanced synthesis techniques, like microwave-assisted methods, improve Ni dispersion and oxygen vacancy formation—key factors for catalytic performance. Findings show that structural modifications and pre-reduction temperature in Ni-La perovskites directly influence CO_2 adsorption and methane production rates, offering insights for designing efficient, sustainable catalysts. This research supports advanced CO_2 utilization technologies crucial for global carbon neutrality efforts.

Preferred and 2nd choice for the topic: Sustainable and clean energy production and transport/CO_2 utilization and recycling
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

In response to global carbon neutrality goals, particularly the European Union's target of achieving carbon neutrality by 2050[1], CO_2 methanation offers a promising pathway to synthesize synthetic natural gas (SNG) within the power-to-gas (PtG) framework. The Sabatier reaction ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$)[2] provides a thermodynamically favourable method to convert CO_2, a greenhouse gas, into valuable methane. However, the reaction is kinetically limited, requiring efficient catalysts to enhance conversion rates[3]. Nickel (Ni)-supported systems are widely studied as active and selective catalysts, owing to Ni's cost-effectiveness and availability[4]. Catalysts based on Ni and non-stoichiometric materials are particularly promising, as oxygen vacancies within these materials play a critical role in CO_2 adsorption, enhancing metal dispersion, and improving resistance to coking[5]. Perovskite structures, in particular, offer excellent oxygen mobility and are resistant to reductive conditions, making them ideal for CO_2 methanation[6]. Previous studies, including work by Grabchenko et al.[7], have demonstrated the superior performance of Ni-La perovskites, with the Ni/$La_2O_2CO_3$ interface playing a significant role in performance, influenced by synthesis methods.

This study evaluates two catalyst structures: lanthanum nickelate prepared via one-pot synthesis and Ni-impregnated lanthanum oxide. Both were synthesized using microwave radiation-assisted (MW) method to improve Ni dispersion and phase uniformity[8]. The results establish key correlations between catalyst structure and CO_2 methanation performance, with a focus on surface species and their impact on reaction rates. Additionally, the study highlights the importance of oxygen vacancies and catalyst reduction in enhancing performance.

Materials and Methods

The one-pot synthesis of lanthanum nickelates was achieved in a single step using microwave radiation-assisted precipitation (MW-OP), employing the corresponding nitrates as precursors. For comparison, lanthanum oxide was prepared using the same procedure and subsequently impregnated with 12 wt.% Ni via the wetness method (MW-Imp). Physicochemical properties were analyzed using XRD, N_2-physisorption, H_2–TPR, and XPS techniques. CO_2 methanation reaction was conducted on partially and fully pre-reduced samples (at 500 and 750 °C for 1 hour under H_2/Ar flow) in a fixed-bed

tubular reactor, with a CO_2 and H_2 gas mixture (1:4 ratio) diluted in N_2. In situ DRIFTS-MS studies were performed reducing the samples at 500 °C or 750 °C in a 10% H_2/Ar stream for 1 hour to evaluate the active phases formed from the reduction treatment. The reaction was monitored by feeding an H_2/CO_2 mixture (4:1 ratio) diluted in argon into the IR cell at 250 °C, allowing for steady-state analysis with spectra recorded every 120 seconds. Effluent gases were analyzed via mass spectrometry.

Results and Discussion

The comparison of XRD patterns of MW-OP and MW-Imp confirmed perovskite-like structures in fresh catalysts, with distinct phases emerging after pre-reduction at 500°C and 750°C (**Figure 1A**), highlighting the influence of synthesis and reduction conditions on catalyst properties. These structural variations impact CO_2 conversion rates, with catalysts containing a higher fraction of perovskite structures demonstrating improved catalytic efficiency. Notably, pre-reducing the catalysts at 500°C preserves Ni-perovskite interfaces, which enhances CO_2 adsorption and conversion, attributed to the unique Ni-La interphase created within perovskite structures (**Figure 1B**). In situ DRIFTS further showed that different active phases formed at each reduction temperature, aligning with the observed improvements in methanation efficiency.

These insights into structure-to-function relationships underscore the critical role of phase composition, Ni dispersion, and oxygen vacancies in optimizing CO_2 conversion.

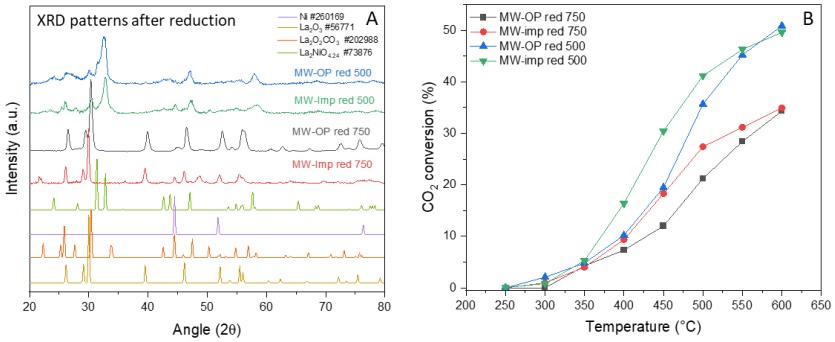


Figure 1 XRD patterns of catalysts after reduction at 500 and 750°C (A), CO2 conversion of the catalysts pre-reduced at 500 and 750°C (B).

References

1. J.C. Navarro, M.A. Centeno, O.H. Laguna, J.A. Odriozola, *Catalysts* **2018**, *8*, 1–25.
2. M. Konsolakis, M. Lykaki, S. Stefa, S.A.C. Carabineiro, G. Varvoutis, E. Papista, G.E. Marnellos, *Nanomaterials* **2019**, *9*.
3. K. Stangeland, D. Kalai, H. Li, Z. Yu, *Energy Procedia* **2017**, *105*, 2022–2027.
4. T.A. Le, M.S. Kim, S.H. Lee, T.W. Kim, E.D. Park, *Catalysis Today* **2017**, *293–294*, 89–96.
5. O.E. Everett, P.C. Zonetti, O.C. Alves, R.R. de Avillez, L.G. Appel, Internation Journal of Hydrogen Energy **2020**, *45*, 6352–6359.
6. M. González-Castaño, J.C.N. de Miguel, A. Penkova, M.A. Centeno, J.A. Odriozola, H. Arellano-Garcia, *Applied Materials Today* **2021**, *23*, 27–30.
7. M. Grabchenko, G. Pantaleo, F. Puleo, O. Vodyankina, L.F. Liotta, *Internation Journal of Hydrogen Energy* **2021**, *46*, 7939–7953.
8. G. Pantaleo, V. La Parola, F. Deganello, R.K. Singha, R. Bal, A.M. Venezia, *Applied Catalysis B : Environmental* **2016**, *189*, 233–241.

Acknowledgements

The Projects “NEST - Network 4 Energy Sustainable Transition” (CUP B53C22004060006), “Capitale Naturale e Risorse per il Futuro dell’Italia (FOE 2020) (CUP B85F21002120005), and PNRR AdP ENEA-CNR (CUP B93C22000630006) are acknowledged for financial support.

Transient isotopic study of low-temperature NO_x reduction by H_2 on $Pt/Mo/ZrO_2$ catalyst

Daniel SCHRÖDER[1], Sven KURETI[1,*]
[1] *Institute of Energy Process Engineering and Chemical Engineering, Chair of Reaction Engineering, TU Freiberg, Fuchsmuehlenweg 9D, 09599 Freiberg, Germany*
** sven.kureti@iec.tu-freiberg.de*

Significance and Relevance

Steady State Isotopic Transient Kinetic Analysis (SSITKA) and in-situ diffuse reflectance infrared spectroscopy (DRIFTS) was used to study the mechanism of low-temperature NO_x reduction by H_2 in lean exhaust gas using highly active $Pt/Mo/ZrO_2$ catalyst [1]. SSITKA clearly shows the participation of adsorbates at the interface around the Pt particles. Moreover, in-situ DRIFTS experiments with isotopic switch from H_2 to D_2 elucidates an additional reaction path toward the formation of N_2 involving NH_x species coordinated to strong acid sites of highly dispersed MoO_x moieties.

Preferred and 2nd choice for the topic:
Fundamental advances in understanding catalysis, Automotive and stationary emission control
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

For NO_x removal from lean automotive exhaust gases, selective catalytic reduction (SCR) and NO_x storage catalysts are established technologies, whereas they operate efficiently only above 175°C. Contrary, future NO_x emissions limits (e.g. Euro-7) will require an effective abatement of NO_x even at low temperatures. For this purpose, the NO_x reduction by H_2 (H_2-deNO_x) on Pt catalysts is a promising technique. However, these catalysts still suffer from significant N_2O and/or NH_3 by-production. Recently, the modification of Pt/ZrO_2 with Mo [1] and W [2] was reported to provide both high activity at low temperatures as well as reduced N_2O and NH_3 emissions. Moreover, enhanced strong Lewis acidity of $Pt/Mo/ZrO_2$ was found to improve N_2 formation, suggesting a highly selective additional SCR-related mechanistic deNO_x pathway [1]. Therefore, this study aims to unravel the reaction mechanism of NO_x reduction by H_2 on $Pt/Mo/ZrO_2$ combining SSITKA and in-situ DRIFTS studies.

Materials and Methods

$Pt/xMo/ZrO_2$ catalysts were prepared by incipient wetness impregnation of monoclinic ZrO_2 with $Pt(NO_3)_2$ (w(Pt) = 0.25 wt.%) and $(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$ (w(Mo) = 0 and 3 wt.%) with subsequent 5h calcination at 500°C. SSITKA experiments were used for in-situ quantification of reactive species in H_2-deNO_x reaction. After rapid switching from ^{14}NO to ^{15}NO by a pneumatic 4-way valve, the evolution of the isotope-labelled products was monitored using an online mass spectrometer. Kr served as inert tracer to correct the gas phase hold-up. Furthermore, in-situ DRIFT spectroscopy enables the identification of adsorbates at the surface of working catalyst. The red shift of the IR bands following the switch from ^{14}NO to ^{15}NO and H_2 to D_2 was used to discriminate reactive from inactive species. All measurements are performed in lean synthetic exhaust gas (200 ppm $^{14}NO/^{15}NO$, 5% O_2, 2000 ppm H_2/D_2, Ar balance, GHSV = 70.000h^{-1}) after reaching steady state at 90°C, 120°C and 150°C.

Results and Discussion

The SSITKA experiment shows a significantly increased number of active species when 3 wt.% Mo is added to the Pt/ZrO_2 catalyst. In particular the amount of N_2 forming intermediates is increased e.g. from 4,3 µmol · g^{-1} to 35,0 µmol · g^{-1} at 120°C, whereas the N_2O-generating species are barely affected.

Table 1. Ratio of active species (SSITKA) to available platinum sites (CO-TPD).

	90°C	120°C	150°C
Pt/ZrO_2	0,7 ±0,9	3,7 ±2,1	7,3 ±1,4
$Pt/3Mo/ZrO_2$	6,1 ±0,6	5,6 ±0,5	1,0 ±0,3

However, for both catalysts the number of active species exceeds the number of available Pt sites (Table 1), suggesting some adsorbates on the support are also involved in the H_2-deNO_x reaction.

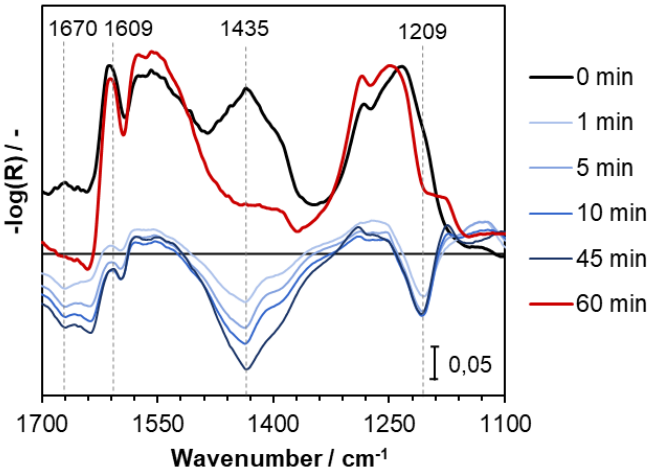


Figure 1. In-situ DRIFTS spectra of $Pt/3Mo/ZrO_2$ after H_2 to D_2 switch, Conditions: 200 ppm NO, 2000 ppm H_2/D_2, 5 Vol.% O_2, Ar Balance, ca. 70.000 h^{-1}.

In-situ DRIFTS experiments show that nitrites are active species on Pt/ZrO_2 as indicated by a 30 cm^{-1} red-shift of ν_{as}(N-O) band at 1190 cm^{-1}. It is assumed that active nitrites are reduced by hydrogen spillover from platinum particles [3]. Although up to 65 ppm NH_3 was detected in the gas phase, no evidence of active NH_x could be found on Pt/ZrO_2 after switch from H_2 to D_2.

In contrast using $Pt/3Mo/ZrO_2$ catalyst, no NH_3 is detected in the gas phase but in-situ DRIFTS experiments show characterristic bands of chemisorbed NH_3 ($\delta_{as}(NH_4^+)$ at 1435 cm^{-1} and $\delta_s(NH_3)$ at 1209 cm^{-1}). More importantly, H_2 to D_2 switch provides evidence that both NH_4^+ and NH_3 coordinated to Lewis acid sites are active for the NO_x reduction below 200°C even in the presence of H_2 (Fig. 1). The strong decline of $\delta_s(NH_3)$ band indicates the particularly high reactivity of NH_3 at the Lewis acid sites (Fig. 2). Additionally, nitrites also appear to be active species on $Pt/3Mo/ZrO_2$ catalyst. Note that the observed decline in IR band intensities of active species is in good agreement with the decay of ^{14}N product observed during SSITKA (Fig. 2).

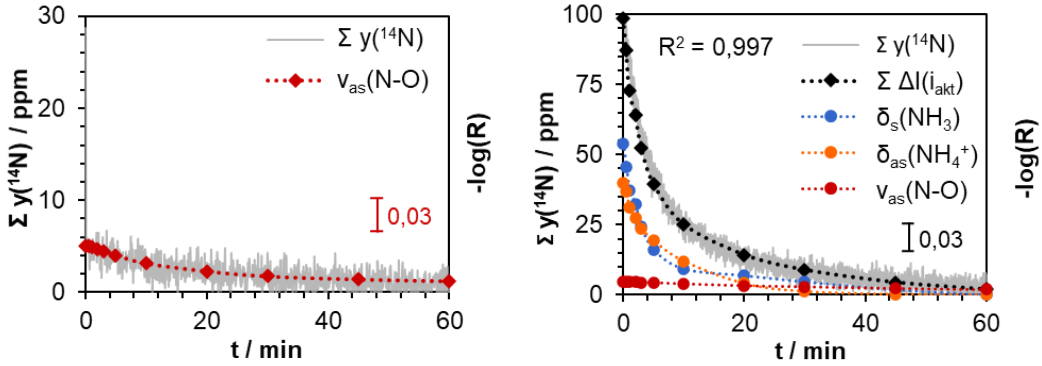


Figure 2. Decline of ^{14}N products (SSITKA) and band intensity of active species after switch from ^{14}NO to ^{15}NO and H_2 to D_2 (in-situ DRIFTS) at Pt/ZrO_2 (left) and $Pt/3Mo/ZrO_2$ (right) at 120°C.

The initial isotope distribution of the products reveals that NO_x reduction by NH_x species is a major reaction pathway for H_2-deNO_x on the Mo promoted catalyst, accounting for about 70% of the total NO_x conversion at 120°C. Finally, initial selectivity of ^{14}N products demonstrates that the reaction of these active adsorbates mainly forms N_2 ($S(N_2) > 80\%$).

The study proves for the first time that the of Pt/ZrO_2 with MoO_x enables an additional reaction pathway of H_2-deNO_x with high N_2 selectivity. In this mechanism ammonia formed on the Pt sites readsorbs on the strong acid sites at highly dispersed MoO_x moieties, followed by a reaction of both NH_3 and NH_4^+ with NO at the interface between the Pt sites and MoO_x. Thus, our study highlights the particular importance of acidity to improve the activity and selectivity of lean H_2-deNO_x catalysts.

References

1. D. Schröder, S. Kureti, *Top Catal* **2023**, *66*, 787–796.
2. E. Eßer, D. Schröder, S. Kureti, *J Catal* **2023**, *423*, 129-144.
3. C. N. Costa, A. M. Efstathiou, *J. Phys. Chem. C,* **2007,** *111,* 3010-3020.

A Parametric Study on Ru-CeO_2 Catalysts for H_2 Production from NH_3 Decomposition

Andrea FELLI[1], Maila DANIELIS[1], Alessandro TROVARELLI[1], Sara COLUSSI[1]
[1]*Politechnical Department, University of Udine, Via del Cotonificio 108, 33100, Udine, IT*
** andrea.felli@uniud.it*

Significance and Relevance

In our study, we carried out a systematic investigation of the parameters that affect the catalytic activity of Ru-CeO_2 catalysts towards NH_3 decomposition. CeO_2 surface area, Ru precursor and Ru deposition method were variated to have several catalysts with different properties. We highlight the relevance of the Ru particles size on the reaction rate, and we find a correlation between the H_2 spillover effect and the reactivity.

Preferred and 2nd choice for the topic: H_2 storage and transportation, green H_2 production, H_2 vectors – Sustainable and clean energy production and transportation
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Ru-CeO_2 is one of the most promising catalysts for H_2 production from ammonia decomposition thanks to the CeO_2 chemical properties and its interaction with Ru[1]. It is then extremely important to understand which properties of this material are more important to enhance the catalytic activity. In this work, we studied several Ru-CeO_2 catalysts prepared via conventional wet impregnation method and with a ball-milling approach. For the first time, we carried out a systematic investigation of the parameters that affect the catalytic activity of Ru-CeO_2 materials towards NH_3 decomposition.

Materials and Methods

Commercial CeO_2 (Rhodia) was calcined at different temperatures (550°C, 800°C, 900°C and 1200°C) for 4h (10°C/min) to obtain supports with a different surface area. Ru acetyl acetonate (RuAA) and Ru black (RuB) in powder form were milled with the different CeO_2 supports in a Pulverisette 23 Minimill for 20 minutes at 15 Hz. Ru nitrosyl nitrate (RuNN) was instead used for the preparation of conventional impregnated materials. All the samples were calcined in air at 550°C for 2h. X-ray diffraction (XRD), N_2 adsorption, H_2-Temperature programmed reduction (TPR), CO_2- Temperature programmed desorption (TPD), CO chemisorption, inductively coupled plasma mass spectrometry (ICP-MS), Raman and DRIFT spectroscopy were used for characterization. NH_3 decomposition was studied by loading 50 mg of sample in a tubular quartz reactor from RT to 550 °C exposed to 30 mL/min of 5% NH_3. A mass spectrometer was used for gas analysis. Reaction rates were calculated by measuring the NH_3 conversion at 270 °C for all the samples.

Results and Discussion

A careful analysis of several parameters was carried out to understand which one mainly affects the NH_3 conversion activity of Ru-CeO_2 catalysts. Interestingly, the specific reaction rate increases as surface area decreases (Figure 1a). This behavior can be ascribable to the formation of very active Ru nanoparticles favored by a low surface area of the support. This is due to the formation of a high number of B5 sites on the metallic surface, that are reported to be extremely active for NH_3 dehydrogenation and N_2 release[2]; the optimal Ru particle size range to maximize B5 sites number is 2-8 nm, which is in good agreement with our findings (Figure 2a). Raman characterization allowed the evaluation of Ru-O-Ce interaction (which is commonly associated with the interaction between the metal and the support), showing how the interaction decreases with the surface area, being negligible on catalysts with the support calcined at 1200 °C (Figure 1c). This is due to the gradual decrease in electron exchange from Ru particles to the support, because of the increase of particle size and the lower surface defectivity of CeO_2. The electronic density of Ru particles is then enhanced in big particles on supports with a lower surface area, favoring the catalytic activity. Generally, RuAA and RuNN

catalysts show a higher H_2 consumption (calculated by TPR analysis) compared to the corresponding RuB samples (Figure 1d); this can be explained by a weaker Ru-H bond strength in RuAA and RuB materials, which enhances the spillover effect and facilitates hydrogen diffusion on the oxide surface[3]. This behavior affects the reactivity since it can help the release of H_2 produced during the reaction, which was individuated as the possible rate-determining step in Ru-CeO_2 catalysts[4], explaining why $RuAACeO_2$ and $RuNNCeO_2$ samples have a higher reaction rate than $RuBCeO_2$.

We can conclude that the deposition method, the Ru precursor, and the CeO_2 surface area strongly influence the specific reaction rate of $RuCeO_2$ catalysts for NH_3 decomposition. We also defined the optimal Ru particle size range to enhance it. The samples with the lower metal-support interaction, and the higher H_2 consumption and spillover effect, are the catalysts with the better reactivity for the reaction.

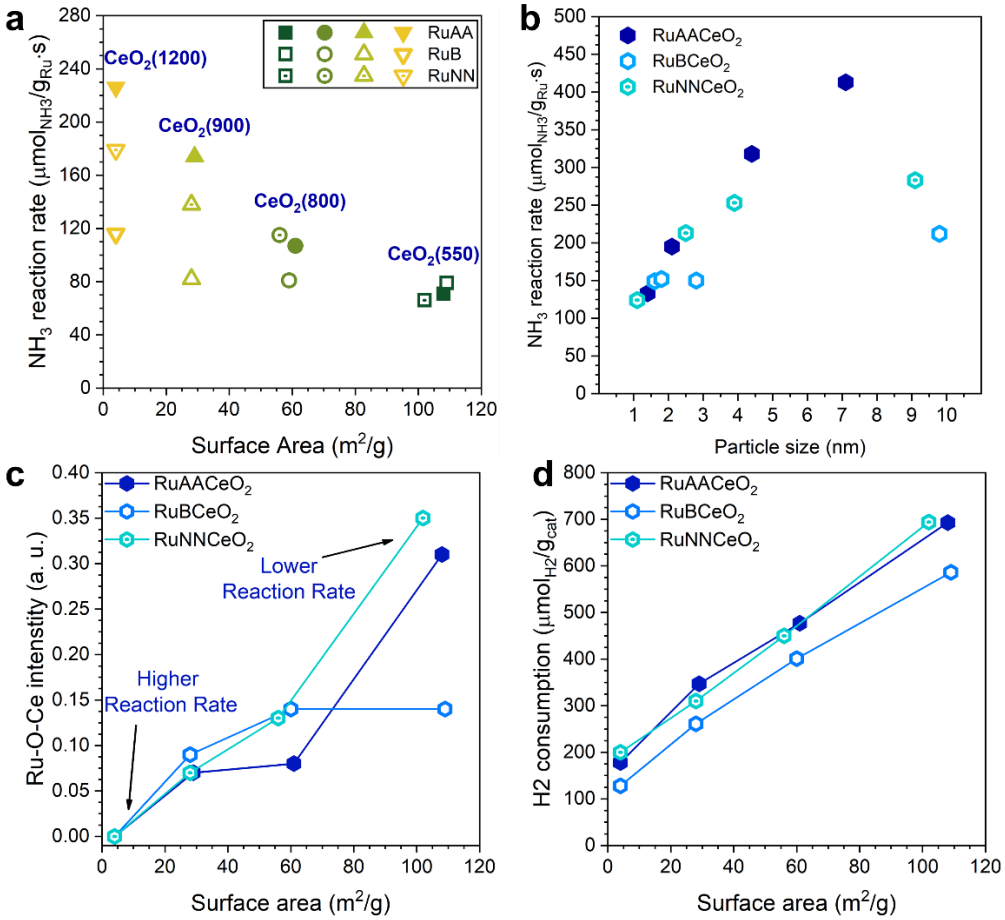


Figure 1 a. NH_3 decomposition reaction rate of $RuAACeO_2$, $RuBCeO_2$, and $RuNNCeO_2$ catalysts as a function of surface area; b. NH_3 reaction rate of $RuCeO_2$ catalysts as a function of Ru average particle size; c. Ru-O-Ce intensity as a function of catalysts surface area; d. Hydrogen consumption as a function of catalysts surface area.

References

1 I. Lucentini, X. Garcia, X. Vendrell and J. Llorca, *American Chemical Society*, 2021, preprint, DOI: 10.1021/acs.iecr.1c00843.

2 F. R. García-García, A. Guerrero-Ruiz and I. Rodríguez-Ramos, in *Topics in Catalysis*, 2009, vol. 52, pp. 758–764.

3 X. Q. Zhang, Y. Q. Qi, H. Liu, J. Y. Wang, L. Y. Xie, J. L. Shi, F. Wang, Y. L. Liu, Z. X. Wang and A. J. Guo, *Chemical Engineering Journal*, DOI:10.1016/j.cej.2024.155203.

4 I. Lucentini, G. García Colli, C. D. Luzi, I. Serrano, O. M. Martínez and J. Llorca, *Appl Catal B*, DOI:10.1016/j.apcatb.2021.119896.

Acknowledgements

Authors are grateful for funding under the REACT EU Italian PON 2014-2020 Program, Action IV.4 – Innovation and Action IV.5 – Green (DM 1062, 10/08/2021).

Fabrication of thermally annealed NiFeS ternary alloy for green hydrogen production

Bernardo PATELLA[1], Salvatore GERACI[1], Roberto Luigi OLIVERI[1], Nadia MOUKRI[1], Giuseppe AIELLO[1], Filippo PELLITTERI[1], Cinzia MURIANA[1], Rosario MICELI[1], Rosalinda INGUANTA[1]

Name presenting Bernardo PATELLA

[1]IUniversity of Palermo, Department of Engineering, Viale delle Scienze, Palermo, Italy

** e-mail corresponding: bernardo.patella@unipa.it*

Significance and Relevance

In this work, we have studied and optimized the fabrication of a ternary alloy of Ni, Fe, and S for H_2 evolution reaction in an alkaline electrolyzer. Particularly, the alloy was fabricated using a template electrosynthesis method in a deposition containing different concentrations of Fe, Ni ions, and S precursor. The composition of the deposition bath was optimized, as well as the deposition parameters (such as potential and deposition time), to obtain a stable and durable alloy. Moreover, the effect of thermal annealing on alloy stability and performance was studied. The optimized electrode has been tested as both anode and cathode. Preliminary results showed a constant potential of -0.4 and 1.6 V vs RHE by applying a constant current density of ±50 mA cm^{-2}.

Preferred and 2nd choice for the topic: H_2 storage and transportation, green H2 production, hydrogen vectors, sustainable and clean energy production and transport
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

In recent years, the use of renewable energy sources has increased more and more[1]. The main drawback of this kind of energy source is the lack of predictability that makes an energy storage system mandatory. The production of green hydrogen using water electrolysis can solve this problem[2].

In this work, we have studied the performance of a novel catalyst for both H_2 and O_2 production in an alkaline electrolyzer. The catalyst was fabricated with nanostructured morphology using cheap and highly active materials, such as iron, nickel, and sulphur[3].

Materials and Methods

The alloy was prepared by template electrosynthesis, using a polycarbonate membrane as a template[4]. To make it conductive, a thin gold layer was sputtered. In the same membrane face, a nickel current collector was electrodeposited. Then, the NWS were deposited into the other membrane face using a Watt's bath modified with $FeSO_4 \cdot 7\ H_2O$ and $Na_2S_2O_3\ 5H_2O$ using the pulsed electrodeposition method. The effect of different concentrations of S precursor and Fe ions in the deposition bath was studied. Finally, the polycarbonate membrane has been dissolved using pure dichloromethane. The annealing process was carried out in a N_2 saturated environment at different temperatures and for different time. The electrodes were characterized using SEM, EDS and XRD analysis. The performances of the electrode for both O_2 and H_2 evolution were evaluated using in a solution of 30% KOH.

Results and Discussion

The electrode fabrication was optimized to obtain a stable array of vertically standing NWs. This kind of morphology allows the obtaining of extremely high surface area and, thus, higher current density for both H_2 and O_2 production. As mentioned in the materials and method section, the concentration of Fe, S, and Ni in the NWs was optimized to obtain this goal. Particularly, the best results have been obtained using a deposition bath made of 0.44 M of Fe ions, 15 g/L of S precursor in the Ni Watt's bath. The annealing process was optimized as well, and the best results were obtained at 500°C for 3 minutes. Figure 1a shows the SEM image of the electrode after the annealing process, and the electrode shows the presence of vertically standing NWs with an average length of about 15 µm. The EDS analysis (Figure 1b) confirmed the deposition of the ternary alloy. The formation of the alloy was also confirmed using XRD analysis.

The optimized electrodes have been tested as both anode and cathode in an alkaline electrolyzer. The counter electrode was a Pt mesh, and a Hg/HgO as a reference electrode. The electrochemical surface area was evaluated by carrying out CVs at different scan rates in a potential range where non-faradic processes occur. These experiments were carried out using the optimized electrode and, for comparison, also a planar Ni strip. Results showed that the proposed electrode has a 10 time higher capacitance compared to the planar one. The same electrodes (NiFeS NWs and Ni strip) were used in a quasi-steady state polarization and results were fitted with Tafel regression. Results showed that the modification of the NiFe alloy with sulfur leads to an improvement in both O_2 and H_2 evolution reactions with a much more remarkable effect on the O_2 evolution reaction.

Finally, the electrodes were used in a short time polarization (6h) using a fixed current density of ±50 mA cm^{-2}. Excellent preliminary results were obtained, with an outstanding stability of potential over time which is around 1.62 and -0.38V vs RHE for O_2 and H_2 production, respectively.

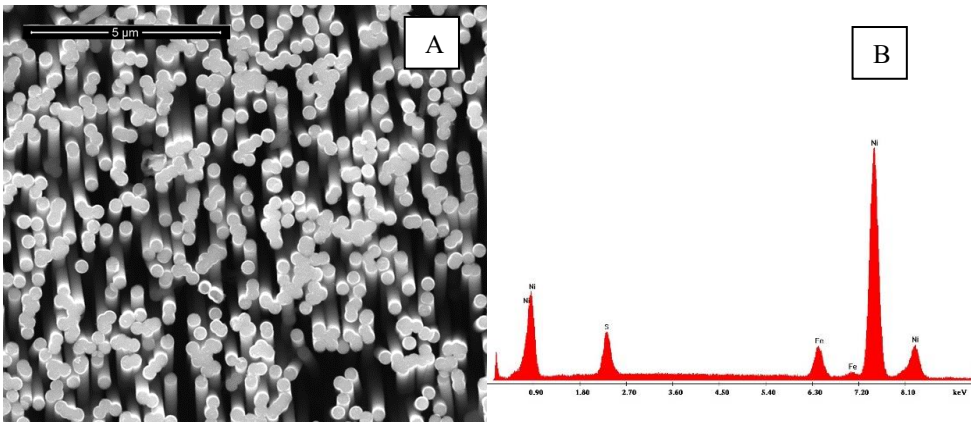


Figure 1 a) SEM image of NiFeS NWs after annealing and corresponding (b) EDS analysis.

Concluding, in the present work we have optimized the fabrication process of a ternary alloy of NiFeS NWs. The electrode was used for O_2 and H_2 production, showing excellent results. Indeed, compared to planar electrodes, the proposed one has a 10 times higher surface area and preliminary galvanostatic experiments showed a very stable potential over 6h of production.

References

1. *A.T.D. Perera, R.A. Attalage, K.K.C.K. Perera, V.P.C.Dassanayake, Energy, 54, 2013, 237-248.*
2. D. Guilbert, G. Vitale, Clean Technologies, 2021, 881-909,
3. F. Safizadeh, E. Ghali, G. Houlachi, International Journal of Hydrogen Energy, 40, 2015, 256–274.
4. S. Carbone, F. Proietto, F. Bonafede, R.L. Oliveri, B. Patella, G. Ganci, G. Aiello, P. Mandin, M. Kim, M. Scopelliti, R. Inguanta, Electrochimica Acta, 2023, 467

Acknowledgments

This work was supported by the Sustainable Mobility Center (Centro Nazionale per la Mobilità Sostenibile—CNMS) under Grant CN00000023 CUP B73C22000760001 Piano Nazionale di Ripresa e Resilienza, Missione 4 - Componente ½

Innovative materials for CO_2 capture and conversion to e-fuels

Marta STUCCHI[*,1], Valentina COLOMBO[1], Alessia COLOMBO[1], Alberto VERTOVA[1], Claudio Ampelli[2], Siglinda PERATHONER[1].

[1]*University of Milano, Chemistry Department, Via Golgi 19, 20133 Milano, Italy.*

[2] *University of Messina, Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, Viale Ferdinando Stagno d'Alcontres 31, 98166 Messina, Italy.*

* marta.stucchi@unimi.it

Significance and Relevance

The general objective of this research is the development of innovative photoelectrochemical devices that incorporate CO_2 capturing from dilute sources and selectively transporting it to electrodes for CO_2 conversion. Specifically, this project aims to realize appropriate electrochemical systems that facilitate the capture of CO_2 and its simultaneous reduction to base products such as methanol (CH_3OH) and ethylene (C_2H_4) for the production of e-fuels, such as dimethyl ether and linear hydrocarbons.

The component capable of selectively capturing and transporting CO_2 consists of metal organic frameworks (MOF) based compounds, and works synergistically with Cu-based materials capable of catalyzing the reduction of CO_2. These materials can be integrated into photoelectrocatalytic devices (PEC), allowing the development of zero-gap flow electrochemical cells, which represent the current development frontier of these devices towards industrial applications.

Preferred and 2nd choice for the topic: **CO_2 utilization and recycling**; **Sustainable and clean energy production and transport**

Preferred presentation: **Short Oral / Poster**

Introduction and Motivations

Carbon Capture and Utilization (CCU) is one of the technologies adopted to simultaneously reduce CO_2 emissions and obtain chemical products or fuels (e-fuels)[1]. Current processes involve the CO_2 capture and purification stages, the "green" H_2 production and the catalytic conversion in one or more stages to e-fuels, making the overall process expensive and inefficient in terms of effective reduction of the carbon footprint[2]. Therefore, the innovative solution that this research aims to develop is based on integrated electrochemical devices, that directly incorporate CO_2 capture and conversion. The goal is directly use the captured CO_2 and sunlight to produce e-fuels through photoelectrocatalytic devices (PEC). In this way devices could operate independently from the availability of electricity from renewable sources, as well as the process costs would be strongly reduced to develop a competitive Solar-to-X (StX) technology that opens new market prospects compared to current e-fuels production technologies.

Results and Discussion

A promising Zr-based MOF system has been selected to be incorporated into a polymeric membrane (Nafion) to obtain a MOF-based mixed matrix membrane (MMM) to be inserted on the gas diffusion side of a porous GDL electrode and a preliminary characterization has been performed. In parallel, proper Cu metal particles and Cu coordination compounds have been prepared to be applied as catalytic components for CO_2 reduction. In particular, complex $[Cu(Neocuproine)_2]^+(PF_6)^-$ has been successfully deposited onto the disk surface (dia=0.5cm) of a GC-RDE (Rotating Disk Electrode) in order to characterize the powder and to study the CO_2 reduction on that material through cyclic voltammetry measurements ranging the potential between -1.5 to 1.6 V vs Reversible Hydrogen Electrode (Fig. 1).

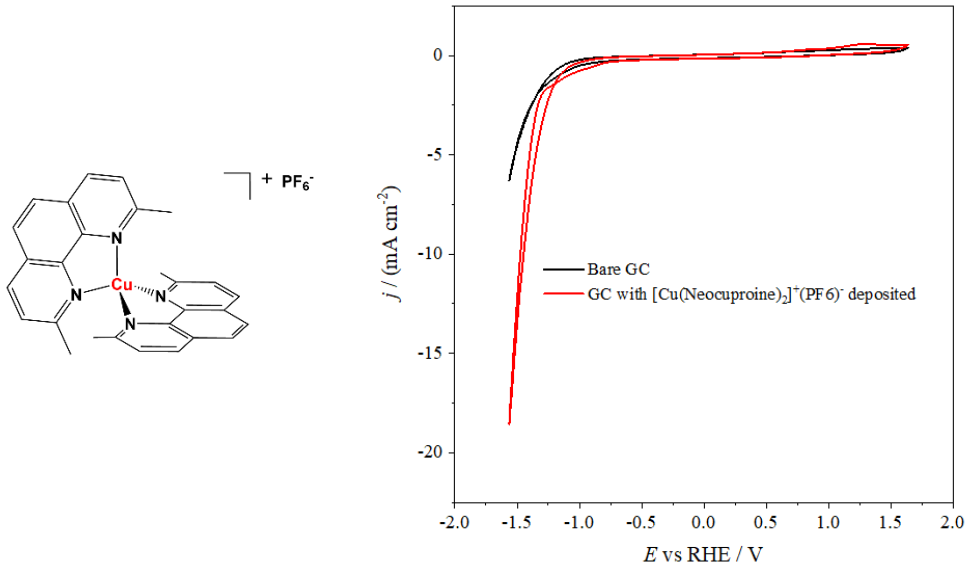


Figure 1 Cyclic voltammetry performed on glassy carbon (black) and on glassy carbon with the copper complex deposited (red) in $NaHCO_3$ 0.1M solution saturated with CO_2

This cyclic voltammetry clearly shows that, by depositing the metal complex, the cathodic current deeply increases, which means an augmented activity toward the reduction of the CO_2 saturated solution. The comparison between activity of the Cu complex with CuO_X nanoparticles showed interesting effects. Then, the GDL electrodes have been evaluated in the electroreduction of CO_2 to methanol, showing preliminary promising results.

References

1. G. Centi, S. Perathoner, *Current Opinion in Chemical Engineering* **2023**, *39*, 100879.
2. P. C. Psarras, S. Comello, P. Bains, P. Charoensawadpong, S. Reichelstein, J. Wilcox, *Environmental Science & Technology* **2017**, *51 (19)*, 11440-11449.

Acknowledgements

This work is part of the project *eCO₂*, supported by the resources of the Spoke 9 – Energy-Sustainable Advanced Materials - financed by the European Union (NextGenerationEU), in the extended partnership NEST - Network 4 Energy Sustainable Transition.

Hierarchical zeolites for methanol and dimethyl ether dehydration into light olefins

Emanuele GIGLIO[*,1], Giorgia FERRARELLI[1], Fabio SALOMONE[2], Elena CORRAO[3], Raffaele PIRONE[2], Samir BENSAID[2], Massimo MIGLIORI[1], Girolamo GIORDANO[1]
[1] *University of Calabria, Dept. of Environmental Engineering, Via Pietro Bucci 45A, 87036 Rende (CS), Italy.*
[2] *Polytechnic of Turin, Dept. of Applied Science and Technology, Corso Duca degli Abruzzi 24, 10129 Turin, Italy.*
[3] *University of Turin, Dept. of Chemistry, Via Pietro Giuria 7, 10125 Turin, Italy.*
** emanuele.giglio@unical.it*

Significance and Relevance

Light olefins have several applications in the chemical industry. To reduce their carbon footprint, they can be produced by dehydration of green methanol or dimethyl ether (DME), that can be synthesized exploiting green H_2 and captured CO_2 through a sustainable and carbon-neutral pathway. Our findings show that a hierarchical structure combined with a milder acidity mitigates the deactivation effects on dehydration catalysts. Thus, a catalyst with strong activity and stability enables more efficient processes, minimizing carbon loss during regeneration and boosting production rates.

Preferred and 2nd choice for the topic: Sustainable and clean energy production and transport / CO_2 utilization and recycling.
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Light olefins, such as ethylene and propylene, are key components for the petrochemical industry. They are conventionally produced via steam cracking of petroleum hydrocarbons; however, light olefins can be alternatively produced via dehydration of methanol or dimethyl-ether (DME) according to the Methanol-to-Olefins (MTO) or the Dimethyl-ether-to-Olefins (DTO) routes[1]. Both methanol and DME can be produced through CO_2 hydrogenation processes starting from green H_2 and captured CO_2.

The dehydration process is generally performed at 300 °C - 450 °C on an acid catalyst (e.g. zeolite); the most investigated materials are SAPO-34 and MFI zeolites. Hierarchical zeolites have recently attracted interest due to lower deactivation rates compared to conventional ones. Their large pores could prevent deactivation, that is commonly related to coke deposition and heavy hydrocarbons formation and may occlude narrow pores. In this work, four different hierarchical zeolites have been synthesized, characterized, and tested to investigate catalytic activity, product distributions and stability over time.

Materials and Methods

On the one hand, two MFI zeolites with a nominal Si/Al ratio of 25 and 50 were synthetized following the procedure reported by Catizzone et al.[2] The crystallization process was carried out at 170 °C for 4 days. Part of these zeolite samples was treated with NH_4^+/HF solution at 25 °C for 6 min under stirring[3]. Then the product was repeatedly washed with distillate water, calcined at 550 °C for 8 hours, ion exchanged and calcined again to reach the H^+-form. The samples were named ETC-25 and ETC-50.

On the other hand, two hierarchical zeolites with a theoretical Si/Al ratio of 25 and 50 were prepared via hydrothermal synthesis[4]. The solution was crystallized in a Teflon lined stainless-steel autoclave at 170 °C for 5 days. Thereafter, the precipitate was separated by means of a centrifuge and washed with water. The obtained sample was dried overnight at 60 °C and then calcined at 550 °C for 5 h. The two samples were labelled HZ-25 and HZ-50.

Both as-prepared and spent samples were characterized by means of several characterization techniques to investigate the crystalline structure, the textural properties and the acidity. In addition, the samples were tested in a fixed bed reactor to evaluate their catalytic performance. The gas was analyzed by using a gas chromatograph equipped with two columns and two detectors for hydrocarbon quantification. The DME conversion profiles were fitted with an Arrhenius-type 1st-order deactivation rate to find the parameters and correlate them to the variation of the material characteristics.

Results and Discussion

The N_2 physisorption of the as prepared samples showed a specific surface area greater than 340 m^2/g for all samples and a bimodal distribution of the pores, meaning that mesopores were formed in hierarchical structures. In addition, the X-ray diffraction proved that all samples have MFI structure. The FT-IR measurements with D_3-acetonitrile as probe molecule showed that the total acidity of ETC-25 and HZ-25 is significantly higher than the acidity of ETC-50 and HZ-50.

Concerning the activity of the samples, Figure 1 presents a comparison of the catalytic performance of a non-hierarchical MFI-25 zeolite and two hierarchical samples (i.e., HZ-25 and ETC-25) tested at 375 °C. The conventional MFI-25 sample is extremely active in DME dehydration, but its performance dramatically dropped during the time on stream[5]. The deactivation was ascribed mainly to coke deposition and heavy hydrocarbons formation. Hierarchical zeolites were indeed less affected by deactivation, and particularly the HZ-25 exhibited a significantly stronger stability. On the contrary, its ethylene production diminished. This phenomenon was ascribed to the different shape and distribution of mesopores that allow larger molecules to diffuse from the particle to the bulk of the gas without trapping them within the inner porosities.

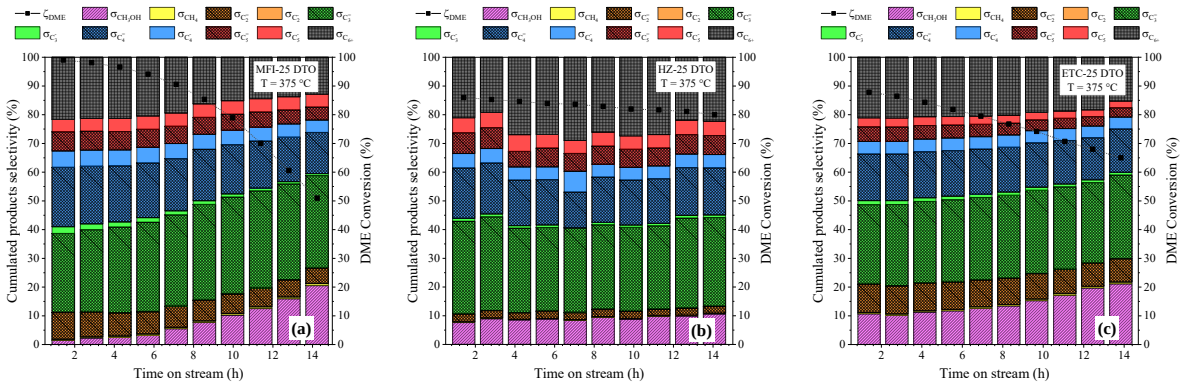


Figure 1. DME conversion and product distribution during DTO tests over time on stream at 400 NL/g/h, 2 bar, 375 °C and 3 vol.% DME/N_2 for (a) MFI-25, (b) HZ-25 and (c) ETC-25.

The acidity reduction (i.e., higher Si/Al ratio) of the MFI-type zeolites improved significantly the stability of the catalysts as summarized in Table 1. This means that the combination of a hierarchical structure and a milder acidity could enhance the total efficiency of the DTO process, reducing carbon losses during the regeneration process.

Table 1. Deactivation parameters of a 1st order deactivation rate for the hierarchical zeolites.

	HZ-25	ETC-25	HZ-50	ETC-50
$k_{d,\infty}$ (h^{-1})	$7.1 \cdot 10^{1}$	$2.6 \cdot 10^{5}$	$1.5 \cdot 10^{-1}$	1.9
$E_{A,d}$ $(kJ\ mol^{-1})$	46.3	83.3	17.2	28.5

References

1. A. S. Al-Dughaither and H. de Lasa, *Fuel* **2014**, *138*, 52-64.
2. E. Catizzone, A. Aloise, E. Giglio, G. Ferrarelli *et al.*, *Catalysis Communications* **2021**, *149*, 106214.
3. Z. Qin, L. Lakiss, J.P. Gilson, K. Thomas *et al.*, *Chemistry of Materials* **2013**, *25*, 2759–2766.
4. C. Wen, J. Jiang, C. Chiliu, Z. Tian *et al.*, *Energy & Fuels* **2020**, *34*, 11282-11289.
5. E. Giglio, G. Ferrarelli, F. Salomone, E. Corrao *et al.*, *Fuel* **2024**, *362*, 130559.

Acknowledgements

F.S. acknowledges the Italian Ministry of University and Research (MUR), program FSE REACT-EU PON Ricerca e Innovazione 2014-2020 (D.M. 1062/2021).

CO_2 hydrogenation activity over iron carbide catalysts having different crystal structures derived from iron oxalate

Akihide YANAGITA, Daisuke KOMIZU, Haruki HORIKOSHI, Keigo TASHIRO, Shigeo SATOKAWA*
Seikei University, Faculty of Science and Technology, 3-3-1 Kichijoji-kitamachi, Musashino-shi, Tokyo 180-8633, Japan.
** e-mail satokawa@st.seikei.ac.jp*

Significance and Relevance

An iron carbide catalyst having χ-Fe_5C_2 structure allows both RWGS and FTS reactions to proceed on a single crystal surface, whereas an iron carbide catalyst having ϑ-Fe_3C structure only allows RWGS. Since the CO production rates and the apparent activation energies of the two catalysts are different, it was inferred that the reaction mechanisms are different with each other due to the differences in the microstructure of the crystal surface.

Introduction and Motivations

Conversion of carbon dioxide (CO_2) to liquid fuels by catalytic reactions is an important technology for realizing a carbon-neutral society. An alkali-containing iron carbide is known as a catalyst that can obtain liquid fuels from CO_2 via reverse water gas shift (RWGS) and Fisher-Tropsch Synthesis (FTS). It has been reported that Fe_3O_4 is the active site for the RWGS reaction and χ-Fe_5C_2 is the active site for the FTS reaction in this catalyst.[1]

We have previously reported that the catalyst with the highest liquid component yield can be obtained by adding 0.8 wt% alkali to χ-Fe_5C_2.[2] This result not only shows that a catalyst with a high liquid component yield has been found, but also that the RWGS reaction also proceeds on χ-Fe_5C_2, and that the Fe_3O_4 phase is not necessary. In this study, we focused on the RWGS reaction occurring on iron carbide and aimed to experimentally prove the difference in activity of iron carbides (χ-Fe_5C_2, ϑ-Fe_3C) for the RWGS reaction proposed in computational study.[3]

Materials and Methods

Catalyst preparation and reaction tests were carried out using a fixed-bed flow reactor. Commercially available iron oxalate dihydrate powder was mixed with quartz sand as a diluent and packed into a reactor, then heat-treated at 350 °C or 500 °C for 4 h under a 30% CO/N_2 gas flow to prepare iron carbide catalysts, FeCx-350 or FeCx-500, respectively. Catalytic activity tests were carried out with a catalyst amount of 0.3 g-Fe, reaction gas composition $CO_2/H_2/N_2$ = 1/3/1, reaction gas flow rate 120-600 mL min^{-1}, pressure 0.1-1.0 MPa(a), reaction temperature 200-320 °C. The outlet gas composition was analyzed using a gas chromatograph equipped with a TCD detector (Agilent 990MCGC).

Results and Discussion

It was confirmed that the FeCx-350 and FeCx-500 were iron carbides with crystal structures mainly composed of the χ-Fe_5C_2 phase and the ϑ-Fe_3C phase, respectively by the XRD analysis. When the RWGS reactivity of each catalyst was evaluated at different reaction temperatures, the selectivity of CO_2 to CO was almost 100%. Since no significant changes were observed in the crystal structure of the catalyst before and after the reaction, it was confirmed that the RWGS reaction proceeds on the surface of iron carbides.

The catalytic activity of each catalyst was compared. FeCx-500 had a higher CO production rate per catalyst surface area than FeCx-350. In addition, the apparent activation energy (*Ea*) was calculated using the Arrhenius plots (Figure 1). The *Ea* values of FeCx-350 and FeCx-500 were calculated to be 92.9 kJ mol^{-1} and 70.4 kJ mol^{-1}, respectively. It was considered that these differences were due to the difference in the reaction mechanism of the RWGS reaction on the ϑ-Fe_3C and χ-Fe_5C_2 crystal surfaces. Effect of reaction pressure for the CO_2 hydrogenation reaction were evaluated. It was found that, the generation of C2-C4 hydrocarbons became prominent as the pressure increased in FeCx-350. On the

other hand, this tendency was not observed in FeCx-500. It was confirmed that the crystal structure of iron carbide has a significant effect not only on RWGS reactivity but also on FTS reactivity.

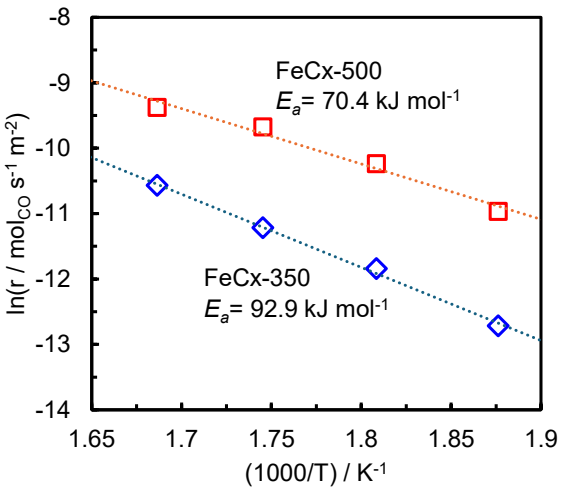


Figure 1 Arrhenius plots of the RWGS reaction over iron carbide catalysts.

References

1. B. Yao, T. Xiao, O. A. Makgae, X. Jie, S. Gonzalez-Cortes, S. Guan, A. I. Kirkland, J. R. Dilworth, H. A. Al-Megren, S. M. Alshihri, P. J. Dobson, G. P. Owen, J. M. Thomas, P. P. Edwards, *Nat. Commun*. **2020**, 11(1), 6395.
2. A. Yanagita, S. Furuya, H. Horikoshi, K. Tashiro, S. Satokawa, *J. Jpn. Petrol. Inst.* **2024**, 67(4), 136-145.
3. S. J. Han, S.-M. Hwang, H.-G. Park, C. Zhang, K.-W. Jun, S. K. Kim, *J. Mater. Chem. A*, **2020**, 8, 13014-13023.

Acknowledgements

This study has been conducted under a contract with the New Energy and Industrial Technology Development Organization (NEDO), Japan. We would like to express our gratitude to NEDO.

Effect of Sulfonation Conditions on Performance of Sulfonated Lignin-Based Porous Carbon Catalyst

Shaohua SHE[1], Shunpei TAKADA[1], Kenji KAMIYA[1], Eika W. QIAN[*,1]
[1]*Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Nakacho, Koganei, Tokyo 184-8588, Japan*
** whqian@cc.tuat.ac.jp*

Significance and Relevance

This study develops lignin-based porous carbon catalysts (LPC) with adjustable sulfonation for efficient cellulose-to-C6 sugar conversion. The optimized LPC-S-200-12 catalyst showed high activity, recyclability, and stability due to its macroporous structure and sulfonic acid retention. Structural stability was confirmed via XPS and XRD. These findings advance understanding of lignin-derived catalysts and address biomass conversion challenges. The novelty lies in optimizing sulfonation conditions and integrating structural characterization to enhance performance and recyclability, driving green chemistry.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion (Preferred choice); Sustainable and clean energy production and transport (2nd choice).
Preferred presentation: Oral preferred or Short Oral / Poster

Introduction and Motivations

The growing demand for sustainable energy and chemicals has highlighted the importance of lignocellulosic biomass as a renewable feedstock for bio-based products. Sugars derived from lignocellulosic biomass serve as critical intermediates in producing biofuels, bioplastics, and other sustainable materials, offering a pathway to reduce reliance on fossil resources.[1,2] However, efficient conversion of cellulose into value-added sugars remains a challenge due to the recalcitrance of biomass and the lack of robust catalytic systems.[3] Lignin, a major component of biomass, has gained attention as a precursor for designing advanced porous carbon materials with tunable properties.[4] By leveraging its unique structure, lignin-based porous carbon catalysts (LPC) offer a sustainable approach to enhance biomass conversion efficiency. This study aims to optimize sulfonation conditions for LPC synthesis, improving catalytic activity, recyclability, and structural stability, with the ultimate goal of advancing green biomass conversion technologies.

Materials and Methods

Preparation of Catalysts

Lignin-based porous carbon catalysts (LPC) were developed using lignin as a carbon precursor and Fe_3O_4 as a template, with sulfonation carried out under controlled conditions. The catalysts, named LPC-S-X-Y and LPC-SCL-X-Y (where X and Y represent the sulfonation temperature in °C and duration in hours, respectively), were synthesized using 98% H_2SO_4 or chlorosulfonic acid (SO_2Cl_2) as sulfonating agents. The synthesis procedure was illustrated in Figure 1.

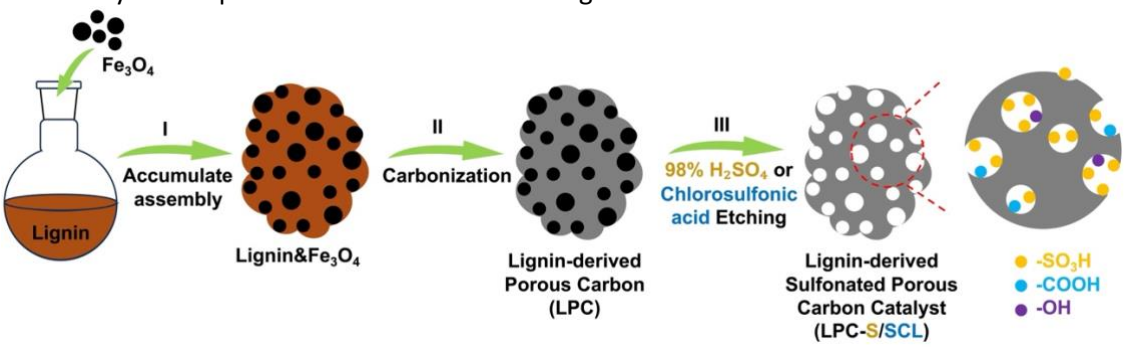


Figure 1 Schematic illustration of the preparation of LPC-S/SCL

Results and Discussion

Morphological of LPC and LPC-S/SCL

The SEM images (Figure 2) reveal distinct morphological features of LPC and sulfonated LPC samples. LPC shows a granular structure with uniform Fe_3O_4 nanoparticles, attributed to lignin adsorption onto Fe_3O_4 during suspension mixing, ensuring effective templating. Sulfonated samples, LSPC-200-12 and LPC-SCL-60-1, exhibit well-developed porous structures with mesopores and macropores. The removal of Fe_3O_4 created a hierarchical pore system. Macropores facilitate the diffusion of large oligosaccharides from cellulose degradation into the pore network, where active catalytic sites are located. This optimization enhances reactant accessibility and catalytic efficiency, emphasizing the importance of macroporosity in LPC-S/SCL performance.

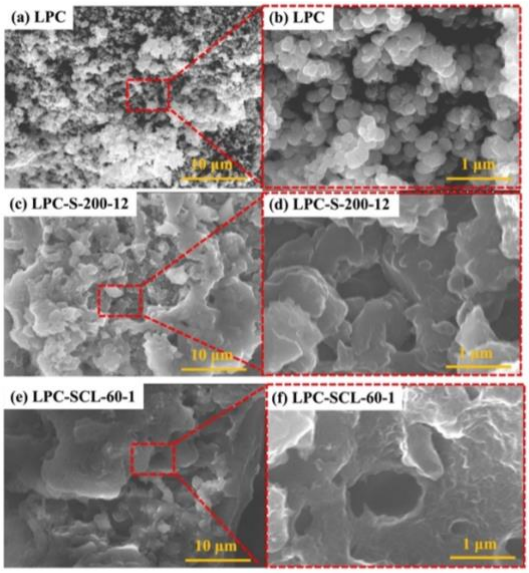


Figure 2 SEM images of (a) and (b) magnified surface structures of LPC; (c) and (d) magnified porous structures of LPC-S-200-12; (e) and (f) magnified porous structures of LPC-SCL-60-1

Catalyst performance and recyclability

The catalytic tests (Figure 3) demonstrate that LPC-S-200-12, synthesized with 98% H_2SO_4 at 200°C for 12 hours, exhibits superior performance in converting cellulose to C6 sugars, achieving the highest liquefaction efficiency among tested catalysts. Durability studies show that LPC-S-200-12 maintains its structural and chemical stability across multiple cycles, outperforming LPC-SCL-60-1 in recyclability. This exceptional performance and stability are attributed to the formation of stable sulfonic acid groups and an optimized pore structure, as confirmed by BET, XRD, and XPS analyses. These results highlight the importance of optimizing sulfonation conditions to enhance catalytic efficiency and long-term performance.

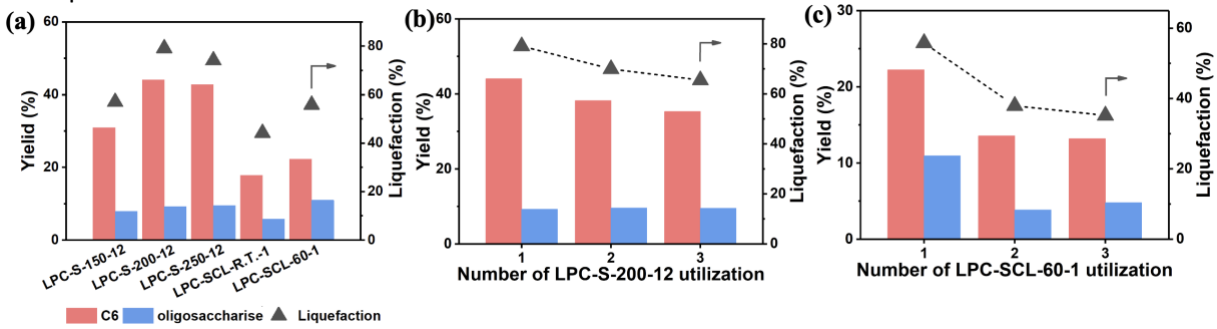


Figure 3 (a) Activity testing of the prepared catalysts;
Durability of (b) LPC-S-200-12 and (c) LPC-SCL-60-1

Conclusion

In summary, LPC-S-200-12, with its optimized pore structure and stable sulfonic acid groups, demonstrates excellent efficiency and durability, highlighting the importance of sulfonation conditions for lignin-derived catalysts in biomass conversion.

References

1. V. Z. Ong, T. Y. Wu, *Renew. Sustain. Energy Rev.* **2020**, *132*, 109924.
2. T. Raj, K. Chandrasekhar, A. N. Kumar, S. H. Kim, *Renew. Sustain. Energy Rev.* **2022**, *158*, 112130.
3. B. Beig, M. Riaz, S. R. Naqvi, M. Hassan, Z. Zheng, K. Karimi, N. T. L. Chi, *Fuel* **2021**, *287*, 119670.
4. M. Yao, X. Bi, Z. Wang, P. Yu, A. Dufresne, C. Jiang, *Int. J. Biol. Macromol.* **2022**, *223*, 980-101

Hydrodeoxygenation of isoeugenol catalyzed by Co/biochar catalyst

Lilia Longo*[1], Davide Baldassin[1], Päivi Mäki-Arvela[2], Joan Wärnå[2], Mark E. Martinez Klimov[2], Olha Yevdokimova[2], Kari Eränen[2], Dmitry Y. Murzin[2], Michela Signoretto[1].

[1] *Ca' Foscary University, Department of Molecular Sciences and Nanosystems, Venice, Italy.*
[2]*Åbo Akademi University, Johan Gadolin Process Chemistry Centre, Henriksgatan 2, 20500 Turku/Åbo, Finland*

** lilia.longo@unive.it*

Significance and Relevance

The hydrodeoxygenation (HDO) of pyrolysis oil is considered a valuable strategy to obtain biofuels. Isoeugenol (IE) is a phenolic compound that is found in bio-oil. The HDO of IE leads to propylcyclohexane (PCH), that has the right features to be used as sustainable jet fuel. For the first time, cobalt based on biochars deriving from the pyrolysis of waste were used as catalysts on isoeugenol hydrodeoxygenation. The best catalytic activity was obtained with Co on biochar derived from rice husk (Co/ARH), which gave total conversion and 55% yield of PCH after 4 hours at 300 °C and 30 bar H_2.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion, Sustainable and clean energy production and transport

Preferred presentation: Oral preferred

Introduction and Motivations

Lignocellulosic biomass (LB) is one of the most important renewable sources for the production of chemicals and fuels. LB utilization requires however some physical or thermochemical transformations, such as fractionation, distillation, pyrolysis, liquefaction, hydrolysis etc[1]. Through catalytic upgrading, such as hydrodeoxygenation (HDO), the liquid fraction of pyrolysis, bio-oil can be exploited as a renewable fuel, for example for the aviation industry[2]. The solid fraction of pyrolysis, biochar, is a renewable carbon based porous material, with a high thermal and chemical resistance that can be used as support for catalysts preparation[3].

Materials and Methods

10 wt. % Co on different biochars were synthesized via wet impregnation, calcined in Ar at 350°C, and reduced in H_2 at 450°C. The materials underwent comprehensive characterization, (N_2 physisorption, CHNS analysis, TPR, NH3-TPD, XRD, SEM, TEM, and XPS). The HDO of IE was explored by varying parameters such as temperature (200–300°C), H2 pressure (10–40 bar), and the catalyst-to-IE ratio in a semi-batch autoclave system (Parr reactor).

Results and Discussion

The characteristics of the carbon support influenced the final catalytic activity, as depicted in Figure 1, with the best results obtained by Co supported on rice husk biochar (ARH). ARH exhibited a hybrid composition of carbon and silica, featuring a hierarchical micro- and mesoporous structure. Co/ARH demonstrated good metal dispersion, the presence of acid sites, and the coexistence of two cobalt phases (Co^0 and CoO). Under optimal conditions, 55% yield of propylcyclohexane was achieved. The kinetic experiments allowed to propose a reaction network, outlined in Figure 1. Recycling tests revealed a slight decline in activity, attributed to organic deposits on the catalyst surface, although the conversion was maintained complete after three cycles (Figure 2).

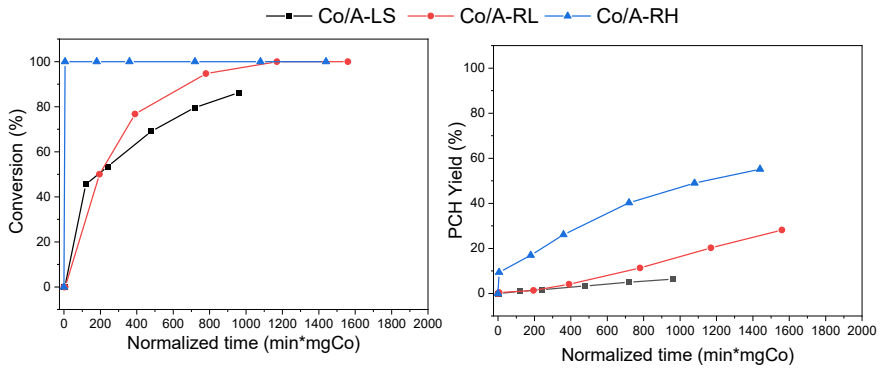


Figure 1 Reaction profiles of Isoeugenol HDO over different catalysts. Reaction conditions: IE 2 mg/mL, dodecane 50 mL, 50 mg cat., 300 °C, 30 bar H_2, 900 rpm, 240 min.

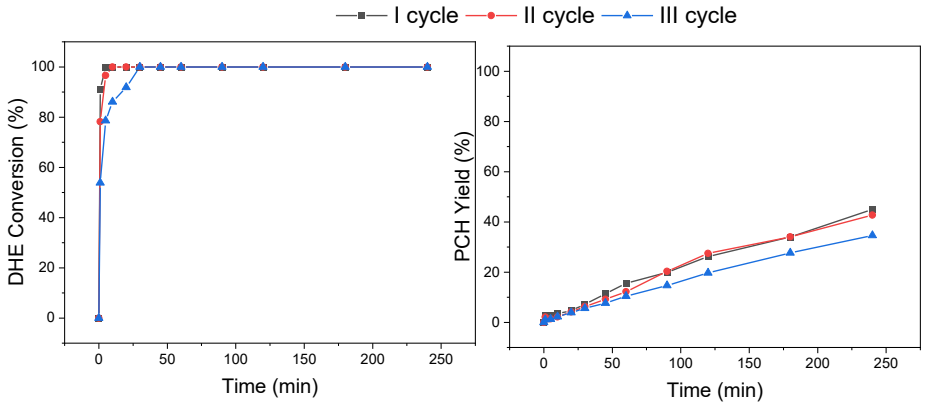


Figure 2 Catalyst recyclability. Reaction conditions: 50 mg Co/A-RH (< 63 µm), dodecane 50 mL, IE 2 mg/mL, 275 °C, 30 bar H_2 900 rpm, 240 min.

References

1. J. Yang, Z. Xing, Q. He, K. Corscadden, H. Niu, *Fuel* **2019**, *237*, 916-936.
2. M. E. Martinez Klimov, P. Mäki-Arvela, Z. Vajglova, M. Alda-Onggar, I. Angervo, N. Kumar, K. Eränen, M. Peurla, M. H. Calimli, J. Muller, A. Shchukarev, I. L. Simakova, D. Y. Murzin, Energy *Fuels* **2021**, *35*, 17755-17768.
3. L. Longo, S. Taghavi, M. Riello, E. Ghedini, F. Menegazzo, A. Di Michele, M. Signoretto, *Catalysis Today* **2023**, *420*, 114038

Acknowledgements

Pasubio SpA and Riseria delle Abbadesse are kindly acknowledged for providing the biomass.
Tania Fantinel is acknowledged for technical support.
Dr. Anssi Peuronen is acknowledged for XRD analyses.
Dr. Alessandro Di Michele is acknowledged for SEM analyses.

Alkali Metal Promotion in Higher Alcohols and Olefin formation from CO_2 Hydrogenation: Shifting the Reaction Mechanism

Renzo A. Leeflang*[1], Sijie Huang[1], Edman S.C. Tsang[1], Guangchoa Li[2]
[1] *Wolfson Catalysis Centre, Department of Chemistry, University of Oxford, Oxford OX1 3QR, United Kingdom*
[2] *Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hong Kong.*
** e-mail renzo.leeflang@chem.ox.ac.uk*

Introduction

In the global effort towards a sustainable society, the circular carbon economy is a tantalizing challenge.[1] Developing a new catalyst capable of converting carbon dioxide into specific products is the key to such a green future. Converting carbon dioxide by renewable hydrogen to higher alcohols (HAs) and olefins is particularly attractive, due to their versatile use in industry and as fuel blends. Achieving this has proven strenuous however. Catalysts for this type of reactions are often designed by combining traditional methanol synthesis metals (e.g. CuZn) and Fischer Tropsch type metals (e.g. FeZn) in the presence of alkali metals (AMs). The combination of Cu and Fe gives rise to a dual site catalyst for dissociative (Fe) and non- dissociative (Cu) CO2 activation at the intersection of which HAs can be formed. The AMs tweak the electronics, structure and hydrogenation ability of the catalyst. Although AMs are widely used[2,3] the difference in promotional effect of K, Rb and Cs on such catalysts is not well documented. Here we explore the superior promotion of Cs over K and Rb in increasing the selectivity to HAs and olefins by studying the role these AMS play in modifying the catalyst structure and opening up a unique CO insertion pathway, which gives rise to both alcohols and olefins.

To this end a series of X-Cu4Zn3Fe3 (X=K, Rb, Cs) catalysts was tested with various AM concentrations. The effect of doping on the catalyst structure and the reaction mechanism are studied extensively using XRD, DRIFTS, H2-TPR, TPD, TPSR, pulse experiments, XPS, XAS and in- situ Mossbauer.

By comparing K, Rb and Cs we shine light on the widely reported, but only superficially understood promotional effect of AMs at the surface of CuZnFe type catalysts.
It was hypothesized that AMs promotion has 2 main effects:

1. Increased carburization leading to increased C-C coupling ability.[4]
2. Increased stabilization of CO species, which can insert into alkyl-chains to form HAs and olefins[5]

Materials and Methods

AM (K, Rb, Cs) promoted Cu4Zn3Fe3 catalysts were synthesized by coprecipitation using metal nitrates at a constant pH (~10) using Na2CO3 and NaOH followed by impregnation using K, Rb or Cs carbonate aqueous solutions. After calcination in air and reduction in 5%H2 the CO2 hydrogenation reaction was performed in a fixed-bed flow reactor at 45 bar at 270- 330°C. Reaction products and conversion were quantified by GC by internal standard method.

Results and Discussion

Doping K, Rb or Cs on our Cu4Zn3Fe3 catalyst shows that Cs is superior to both Rb and K increasing the selectivity of CO2 hydrogenation to HAs (13, 12 and 10% respectively) whilehaving a limited effect on conversion. Olefin selectivity is similar between K and Cs (36%) and is lower for Rb (30%). For undoped samples alcohols are 1.3 and olefins 0% showing the remarkable influence of AMs on the catalytic behavior.

Additionally the selectivity of hydrocarbons of carbon number higher than 4 increases for doped

samples. However, at higher AMs concentrations, CO selectivity increases as well. Most strikingly, Cs is greatly superior in the suppression of CO formation favoring coupled products at all concentrations tested.

As expected, AM doping promoted carburization as indicated by XRD, XPS, XAS and Mossbauer. In effect, the AMs are able to induce a phase separation of the CuFeOx spinel phase during reaction, thereby ensuring the formation of metallic Cu and carburized Fe phases.
Interestingly, the catalytic behavior of these catalysts is also significantly affected before carburization as indicated by a stronger adsorption of CO as measurement by DRIFTS and TPSR. Surprisingly, the K doped catalyst stabilizes CO more than Rb and Cs, despite its (in principle) lower alkalinity. Additionally it shows an increase in particularly strongly rather than medium adsorbed CO. This may account for its overall higher CO selectivity during catalysis. We speculate that this difference between K, Rb and Cs is due to their different local environments.

In contrast to the general literature, we propose that the effect of AMs is not chiefly derived from the ability to suppress the hydrogenation ability, but rather is primarily based on facilitating CO insertion. Hereby both alcohols and olefins share an reaction pathway: CO is inserted into an alkyl chain and hydrogenated to HAs, which can either desorb to give HAs or dehydrate to form olefins. This is in line with our ethylene hydrogenation pulse experiments, which show no clear trend when comparing our different catalysts, while ethanol dehydration experiments and in-situ DRIFTS clearly show the viability of this reaction pathway over AM promoted catalysts.

Significance

The catalytic conversion of CO_2 to specific products is essential to establishing a circular carbon economy. To be able to establish such economy catalyst with a high degree of selectivity towards desired products are required. Considering the wide use of higher alcohols and olefins in industry it is imperative to have catalysts capable of synthesizing them from CO_2 and H_2.

In order to move away from trail-and-error based research into rational design a detailed understanding of the interaction between catalysts and dopants is required. Alkali metal doping of CO_2 hydrogenation catalysts is widely employed, but the literature lacks a comprehensive understanding of their role on the reaction mechanism. Our research shines a light on the unique role of AMs on the reaction mechanism of CO2 hydrogenation.

References

1. L. M., Alsarhan, A. S. Alayyar, N. B Alqahtani, N. H Khdary, *MPDI*. **2021**. *13(21),* 11625
2. D. Xu, M. Ding, X. Hong, G. Liu, S.C.E Tsang, *ACS Catal*, **2020**, *10 (9)*, 5250–5260
3. S. Li, H. Guo, C. Luo, H. Zhang, L. Xiong, X. Chen, L. Ma*, Catal. Lett*., **2013**, 143, 345–355
4. N. Fischer, R. Henkel, B. Hettel,M. Iglesias; G. Schaub, M. Claeys, *Catal. Lett.* **2016**, 146 (2), 509–517.
5. X. Wang, P. J. Ramírez, W. Liao, J. A. Rodriguez, P. Liu, *J. Am. Chem. Soc.* **2021**, *143* (33), 13103–13112.

Design of novel inverse ZrO_2/Ni catalysts for CO_2 utilization: from CO_2 to syn-methane

Li Li [1,2], Patrick DA COSTA[*,2], Changwei Hu[*,1]
[1] *Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, China.*
[2] *Institut Jean Le Rond d'Alembert, Sorbonne Université, CNRS UMR 7190, 2 place de la gare de ceinture, Saint Cyr L'Ecole, France.*
* *patrick.da_costa@sorbonne-universite.fr*
changweihu@scu.edu.cn

Significance and Relevance

The metal-oxide (M-O) interface is crucial in catalysis by guiding the design of highly active catalysts. Unlike conventional catalysts, inverse-phase catalysts load small, inert oxide nanoparticles onto larger, active metal substrates, emphasizing the importance of the O-M interface. In this work, we employed inverse ZrO_2/Ni catalysts for CO_2 methanation, achieving for the first time a unique ZrO_2-Ni interfacial structure. This novel approach led to an enhancement of the catalytic performance and stability of the designed catalyst, providing new insights into interfacial interactions that can improve CO_2 methanation efficiency.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling, Sustainable and clean energy production and transport

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

CO_2 methanation is the most promising and mature route for CO_2 utilization, converting greenhouse gases into valuable fuels and addressing environmental concerns[1]. The catalytic efficiency and stability of Ni-based catalysts in this reaction are influenced by the interaction between metal and oxide phases[2]. In conventional M/O catalysts, the migration of oxides to the surface of the loaded active metal requires high temperatures, resulting in an uncontrollable cover layer, which may make it difficult to distinguish the individual roles of the various O-M interfaces in M/O catalysts[3]. Recent studies suggest that inverse catalysts, where inert oxide nanoparticles are loaded onto active metal surfaces, can enhance catalytic performance by optimizing interfacial properties[4]. This study explores the potential of inverse ZrO_2/Ni catalysts in improving CO_2 methanation efficiency.

Materials and Methods

The inverse ZrO_2/Ni catalysts were synthesized via the impregnation method. A series of characterization methods including BET, XRD, (HR)TEM, H_2-TPR, CO_2-TPD, XPS and *in-situ* DRIFT were carried out to investigate the physicochemical properties of the catalysts.

Results and Discussion

A series of inverse ZrO_2/Ni catalysts with varying Zr/Ni were synthesized and systematically characterized. Figure 1 highlights the catalytic activity results, where the $70ZrO_2$/30Ni catalyst demonstrated exceptional performance, achieving a CO_2 conversion of up to 75% and CH_4 selectivity of 99.7% at 250°C. This catalyst also showed excellent stability, with no observable deactivation over extended reaction times, as illustrated in Figure 2. Comprehensive catalyst characterization revealed that the superior activity of $70ZrO_2$/30Ni is attributed to its larger specific surface area, a higher concentration of medium-strength basic sites, an increased Ni^0 ratio, and a greater concentration of oxygen vacancies, along with enhanced dispersion of ZrO_2 on the NiO support. Additionally, *in situ* DRIFTS analysis confirmed that CO_2 methanation mechanism on these catalysts proceeds via the formate route across all samples. These findings underscore the critical role of metal-oxide interactions in achieving high CO_2 conversion and selectivity, advancing the design of effective inverse catalysts for CO_2 methanation.

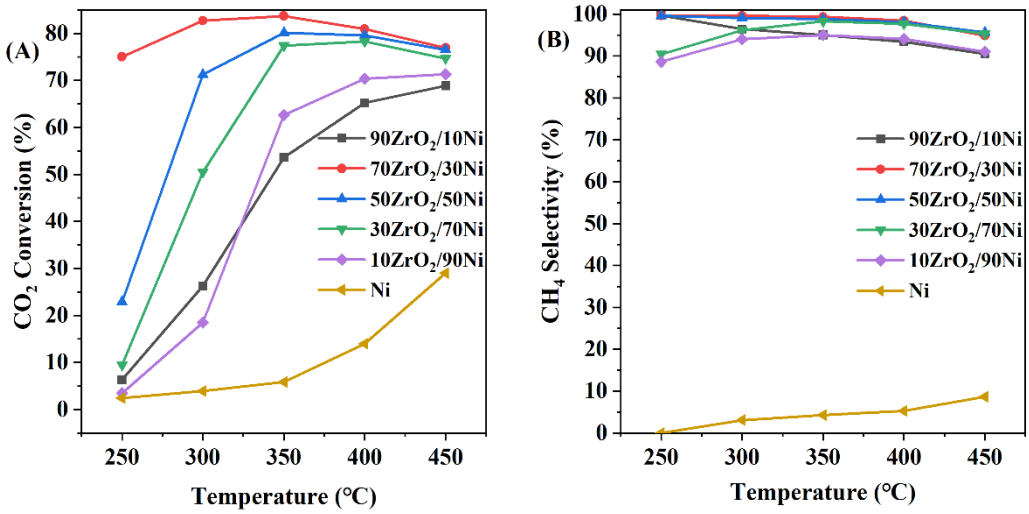


Figure 1 The catalytic activity of different inverse ZrO_2/Ni catalysts (A) CO_2 conversion and (B) CH_4 selectivity (GHSV=30,000 h^{-1}, reduction 1h, 550 ℃)

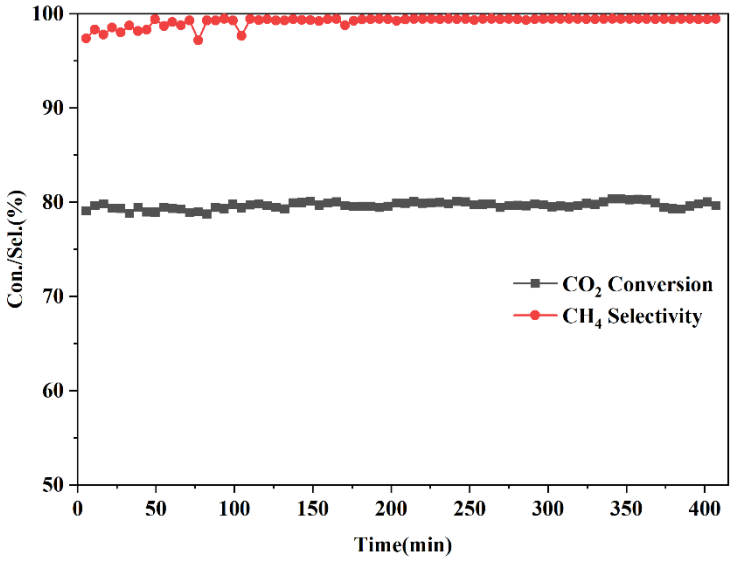


Figure 2 The catalytic stability of 70ZrO_2/30Ni at 300℃ (GHSV=30,000 h^{-1})

References

1. Z. Yuqi, M. Xiaoling, Chemical Engineering Journal **2024**, 485, 149937-149949
2. Z. Jing, M. Will, Surface Science Reports **2018**, 73, 117-152.
3. R. José A, L. Ping, The Journal of Physical Chemistry Letter **2016**, 7, 2627−2639.
4. T. Junbo, Z. Peng, Applied Catalysis B: Environmental **2023**, 339, 123121-123133.

Acknowledgements

Funding: National Natural Science Foundation of China (No. 22472109), 111 center (No. B17030), the Fundamental Research Funds for the Central Universities.

Storage element – catalyst interaction on different supports for cyclic CO_2 capture and methanation

Giuseppe NAVA[1], Alessandro PORTA[1], Roberto MATARRESE[1], Carlo Giorgio VISCONTI[1], Luca LIETTI[1]*
[1]*Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano – Via La Masa 34, 20156 Milan, Italy*
** luca.lietti@polimi.it*

Significance and Relevance

Dual Functioning Materials (DFMs) for integrated CO_2 capture and methanation are a promising technology for the recycling of CO_2 utilizing green H_2 (Power-to-SNG). In this work, we prepare and compare different DMFs, highlighting synergistic (or detrimental) interaction between the storage element and hydrogenation metal over different supports.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling
Preferred presentation: Oral preferred

Introduction and Motivations

CO_2 plays a central role in the energy transition: different catalytic processes for its hydrogenation into valuable products are gaining momentum, including production of methane, methanol or sustainable aviation fuels (SAF). The catalytic conversion of CO_2 requires a concentrated CO_2 feed, which can be obtained by capturing CO_2 from air or point sources using a liquid or solid sorbent. However, the regeneration of the sorbent is energy intensive, and the separated CO_2 must be typically stored and transported to a conversion facility. Dual Function Materials (DFMs) have been proposed to increase the efficiency of the CO_2 capture and conversion process: by coupling a storage element with a hydrogenation catalyst it is possible to cyclically capture CO_2 from air or flue gases and reduce it to valuable products upon renewable H_2 exposure. For flue gases applications, where CO_2 is available at near atmospheric pressures and temperatures ranging from 150 - 350°C, CH_4 is the preferred target.

Coupling the storage element and the catalytic one over the same support is not necessary, but when using Al_2O_3 as a support a synergistic effect was observed[2], leading to increased CH_4 formation. In this work we prepare and compare different capture and methanation materials obtained by supporting the storage and catalytic elements on the same support particle, or by physically mixing two different materials.

Materials and Methods

DFMs are prepared through Incipient Wetness Impregnation starting from a commercial TiO_2 (Norpro). Al_2O_3 (Sasol) or SiO_2 (BASF). Sodium Carbonate (Alfa Aesar) or Barium Acetate (Sigma Aldrich) are used as storage element. This and/or Ru nitrosyl nitrate (Alfa Aesar, 32%) are impregnated over the support, dried and calcined at 500 °C. The materials are characterized by BET, XRD, SEM-EDS, H_2 chemisorption, CO_2 adsorption followed by TPD or H_2-TPSR.

The performance of different materials is assessed by comparing the activity of the mechanical mixture (e.g. Na/TiO_2 + Ru/TiO_2) with that of the DFM (e.g. $Ru/Na/TiO_2$), keeping constant the amount of storage and catalytic element within the microreactor. The materials are tested under cyclic conditions, comprehensive of a capture phase (1% CO_2, 5 min), a purge phase (He, 5 min) and a methanation phase (4% H_2, 5 min) at different temperatures (250-350 °C). Gas phase is monitored using a mass spectrometer, an FT-IR analyzer and a micro-GC. The same methodology is used for testing under simulated flue gas conditions, adding 3% O_2 and 2% H_2O during the adsorption phase. A final heating in presence of H_2 is performed at the end of each experiment to quantify the unreacted adsorbed CO_2. Selected experiments are replicated in an *operando* FT-IR set-up to obtain mechanistic information.

Results and Discussion

Preliminary results over bimetallic Ru-Na/TiO_2 cycled at 350°C provide a fast methane production in correspondence of the first seconds of the isothermal methanation phase. However, residual CO_2 remains adsorbed on the catalyst surface at the end of the hydrogenation phase. Interestingly, when the mechanical mixture of Ru/TiO_2 and Na_2CO_3/TiO_2 is tested in the same experimental condition, CH_4 production during the isothermal cycle is significantly higher by 3 times with respect to what observed in the case of the bimetallic Ru-Na/TiO_2, due to a CO_2 storage capacity at 350 °C which is nearly 3 times higher that that measured using the bimetallic Ru-Na/TiO_2. This indicates a detrimental effect of the vicinity of the storage and catalytic metal, which is not observed for Al_2O_3-supported catalysts[2], for which a synergistic effect is observed between the CO_2 storage capacity and the methanation activity. Additional catalytic tests and operando characterization is currently ongoing to provide mechanistic explanation for this behavior.

1. C. Jeong-Potter, A. Porta, R. Matarrese, C. G. Visconti, L. Lietti, R. Farrauto, *Applied Catalysis B*, **2022**, 310, 121294.
2. A. Porta, C. G. Visconti, L. Castoldi, R. Matarrese, C. Jeong-Potter, R. Farrauto, L. Lietti, *Applied Catalysis B*, **2021**, 283, 119654.

Acknowledgements

Authors would like to thank MIAMI "Materiali Innovativi per Sistemi di Accumulo Ibrido" (CSEAA_00014) for economical funding.

CO_2 activation dictates catalytic performance on different CeO_2 morphologies in the low temperature DRM reaction

Petar Djinović[1,2], Kristijan Lorber[*,1]
[1]*National Institute of Chemistry, Ljubljana, Slovenia.*
[2] *University of Nova Gorica, Nova Gorica, Slovenia.*
** Kristijan.lorber@ki.si*

Significance and Relevance

- Catalytic efficiency in terms of activity and stability over different CeO_2 morphologies was investigated by ex- and in-situ methods.
- Investigation of nature and amount of accumulated carbon during the DRM reaction.
- Activation of the CO_2 effects on the removal of the accumulated carbon during the DRM reaction.
- Interactions between CO_2 and different CeO_2 morphologies were investigated by in-situ DRIFTs measurements combined with mass spectrometry.
- Whit the correlation of in-situ measurements results and theoretical DFT calculations, the tentative mechanism for CO_2 activation on a reduced CeO_{2-x} surface was proposed.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling; Fundamental advances in understanding catalysis
Preferred presentation: Oral or Short Oral / Poster

Introduction and Motivations

Dry reforming of methane (DRM) offers an effective approach to mitigate greenhouse gas emissions by converting methane (CH_4) and carbon dioxide (CO_2) into syngas (H_2 and CO), a vital feedstock for various industrial applications.[1] The choice of catalyst and the morphology of its support significantly influence catalytic efficiency, carbon deposition, and overall stability.[2] This study examines the impact of different exposing surface crystal planes of CeO_2 nanostructures (nanorods CeO_2-R, nanocubes CeO_2-C, and nanospheres CeO_2-S) on the catalytic performance and stability of Ni/CeO_2 catalysts in DRM.

Materials and Methods

The CeO_2 nanorods and nanocubes were synthesized through a hydrothermal process, while nanospheres were prepared using the surfactant CTAB.[3] Nickel was deposited in varying weight fractions on ceria supports, and catalytic testing was conducted at temperatures between 400 and 500 °C. The analysis of adsorption sites and CO_2 activation on the pre-reduced catalysts provided insights into their catalytic mechanisms.

Results and Discussion

The morphology of CeO_2 significantly affects catalytic activity and carbon deposition. CeO_2 nanorods showed the highest CH_4 and CO_2 conversion rates, with 2Ni-R catalysts outperforming other examined morphologies. CeO_2-C exhibited the strongest CO_2 adsorption sites, influencing carbon deposition rates, while CeO_2-S accumulated the least carbon due to limited accessibility of the active Ni sites. Across all three CeO_2 structures, predominantly 1 nm nickel clusters (estimated from in-situ XAS) coexisted with Ni crystals around 6 nm in diameter (as observed by TEM). The polydentate carbonate species primarily populate the {100} facet of ceria, characteristic of the nanocube surface, while monodentate and bidentate carbonates prevail on the {111} facet. The thermally stable polydentate carbonate, covering a significant portion of the partially reduced ceria surface, reacts slowly with H_2 and behaves as a spectator species rather than an active participant in DRM at 500 °C.

Overall, CeO_2 nanorods emerge as promising candidates for enhancing DRM activity and stability, demonstrating high activity and lower carbon deposition tendencies. These findings offer valuable insights for the development of advanced Ni/CeO_2 catalysts tailored to sustainable syngas production, supporting further progress in efficient and environmentally friendly energy conversion technologies.

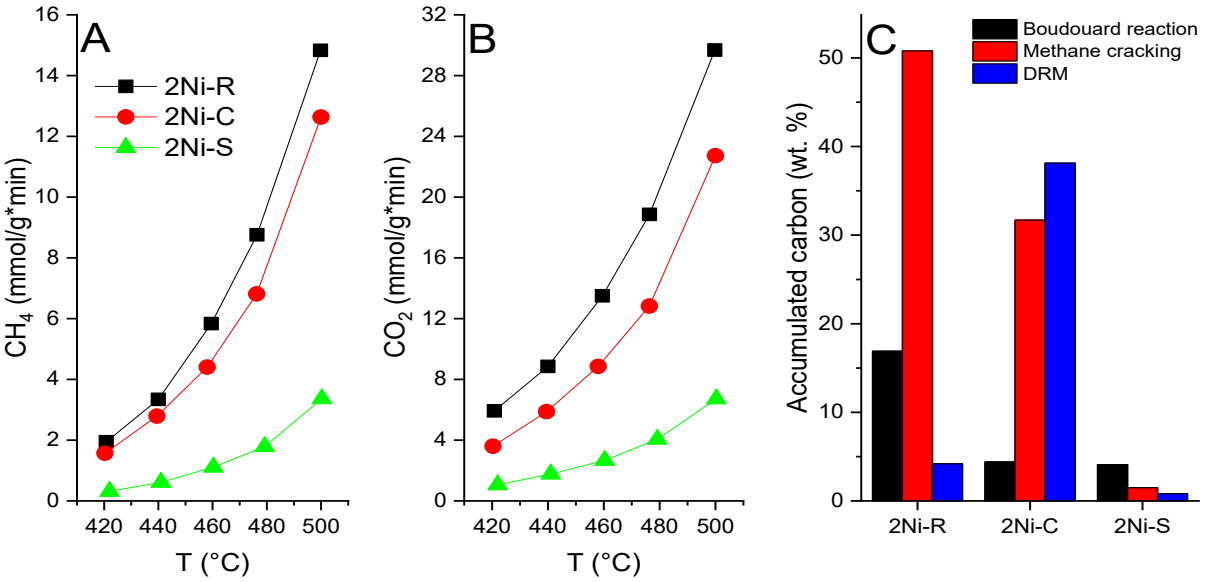


Figure 1. The reaction rate for (A) CH_4 and (B) CO_2 as a function of temperature for 2Ni-R, 2Ni-C and 2Ni-S catalysis. (C) Carbon accumulated over 2Ni-R, 2Ni-C and 2Ni-S catalysts during 1 h of TOS in methane cracking and the Boudouard reaction, and 6 h of TOS during DRM at 500 °C.

References

1. P. Jagadeesh, et al., A short review on recent advancements of dry reforming of methane (DRM) over pyrochlores, Mater. Today Proc. 72 (2023) 361–369.
2. N.A.K. Aramouni, et al., Catalyst design for dry reforming of methane: Analysis review, Renew. Sustain. Energy Rev. 82 (2018) 2570–2585.
3. K. Lorber, et al., CO_2 Activation over Nanoshaped CeO2 Decorated with Nickel for Low-Temperature Methane Dry Reforming, ACS Appl. Mater. Interfaces. 14 (2022) 31862–31878.

Acknowledgements

PD and KL acknowledge Slovenian Research Agency (ARIS) for financial support through programs P2-150, P1-0021 and project J2-1726.

Dual-Function Bi-Based Electrodes for Coupled CO_2 Reduction and Glycerol Oxidation

Shokouh Masoumi[1], Zohreh Masoumi[1], Daeseung Kyung[*,1]
[1] *Department of Civil and Environment Engineering, University of Ulsan, Daehakro 93, Namgu, Ulsan 44610, Republic of Korea*
* dkyung@ulsan.ac.kr

Significance and Relevance

These Bi-based electrodes enable simultaneous electrochemical CO_2 reduction (CO_2RR) and glycerol oxidation (GOR), leveraging a dual-function catalytic system that increases efficiency and selectivity for both reactions. These electrodes enhance the catalytic pathway for CO_2-to-formate conversion and effectively utilize GOR alongside CO_2RR. These electrodes are used in a single reaction system, and to our knowledge, this is the first time they are utilized in dual-function systems, which enhance reaction performance. Coupling GOR with CO_2RR is an efficient way to use a waste byproduct (glycerol, from biodiesel production) while generating valuable chemicals like formate. This integrated approach aligns with circular economic principles by combining waste utilization and chemical synthesis.

Preferred and 2nd choice for the topic: Integrated CO_2 Reduction and Glycerol Oxidation on Bi-Based Electrodes for Enhanced Efficiency as A Sustainable Approach
Preferred presentation: Poster presentation

Introduction and Motivations

The simultaneous electrochemical reduction of CO_2 and oxidation of glycerol presents a sustainable pathway for producing valuable chemicals while addressing CO_2 emissions and waste glycerol utilization from biodiesel production[1]. Traditional CO_2 reduction systems often suffer from high energy demands and limited selectivity but coupling it with glycerol oxidation offers enhanced reaction efficiency and selectivity for desired products[2]. Recent studies on Bi-based catalysts have shown promising performance, particularly in stabilizing intermediates critical for selective formate production, motivating the development of dual-function systems for improved catalytic performance[3].

Results and Discussion

In this study, Bi_2S_3 nanoplates were synthesized on copper foam and electrochemically reduced to Bi nanoplates, which showed strong adherence to the substrate and high selectivity for formate ($HCOO^-$) production during CO_2 reduction. The Cu foam/Bi catalyst achieved a high Faradaic efficiency at a low overpotential. In an electrochemical system, this catalyst was paired with a modified $BiVO_4$ photoanode for glycerol oxidation, enabling simultaneous CO_2 reduction and glycerol oxidation under simulated solar irradiation. This research highlights the potential of Bi_2S_3-derived Bi nanoplates on copper foam as effective dual-function catalysts for CO_2 reduction and glycerol oxidation. The findings showcase the catalyst's stability and selectivity, paving the way for sustainable CO_2 utilization and the use of waste glycerol as a co-reactant in integrated electrocatalytic systems.

References

1. J. R. C. Junqueira, et al. ChemSusChem 2023, 16, e202202349.
2. A. Kormányos, et al. ACS Catal. 2024, 14, 9, 6503–6512
3. B. van den Bosch, et al. ChemPlusChem 2023, 88, e202300112

Acknowledgements

This work supports by "Regional Innovation Strategy (RIS)" through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (MOE) (2021RIS-003), and the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (RS-2024-00343746).

CO_2 cycloaddition to limonene diepoxide: catalysis, kinetics and mass transfer

Federica ORABONA[*,1,2], Stefano NAPOLITANO[1,2], Veronika D. BADAZHKOVA[2], Wander PEREZ-SENA[2], Kari ERÄNEN[2], Martino DI SERIO[1], Dmitry MURZIN[2], Vincenzo RUSSO[1,2], Tapio SALMI[1,2]

[1]Università di Napoli 'Federico II', Chemical Sciences, IT-80125 Napoli, Italy
[2]Åbo Akademi, Laboratory of Industrial Chemistry and Reaction Engineering (TKR), FI-20500 Turku/Åbo, Finland
** federica.orabona@abo.fi*

Significance and Relevance

In this work, the reaction kinetics and mechanism of the CO_2 cycloaddition of limonene diepoxide as well as the mass transfer of CO_2 as a function of the conversion, temperature and pressure have been unveiled for the first time. The reaction proceeds via a consecutive mechanism in the presence of homogeneous and grafted catalysts via the formation of a mono-carbonate intermediate. The final product, i.e. limonene dicarbonate can find application as a building block for the synthesis of isocyanate-free polyurethanes.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling, Green chemistry and biomass transformation
Preferred presentation: Oral preferred

Introduction and Motivations

Limonene is an abundant and cost-effective renewable chemical with a global annual production of approximately 70 kt (2017). Thanks to its very special chemical structure, it can be further functionalized to obtain different monomers for the production of biomaterials[1]. For instance, limonene diepoxide is a promising precursor for the synthesis of non-isocyanate polyurethanes (NIPU). The catalyzed cycloaddition of CO_2 to limonene diepoxide produces a bifunctional five-membered cyclic carbonate i.e., limonene decarbonate (LDC) which is particularly interesting as the precursor of NIPU[2].

In this work, the carbonation of limonene diepoxide was performed in a stainless-steel reactor autoclave (Parr) under solvent-free conditions, at relatively high temperatures and CO_2 pressures and in the presence of homogeneous and heterogenized catalysts. Different quaternary ammonium salt halides were tested both in the homogeneous phase and grafted on SiO_2-based supports, and very precise kinetic studies were conducted with the best catalyst by varying the operating parameters. The solubility of CO_2 in the reaction medium was measured at different temperatures and pressures and the gas-liquid mass transfer coefficients were evaluated.

Materials and Methods

The carbonation of limonene diepoxide (LDO, Nitrochemie), was performed in a stainless-steel reactor autoclave (Parr) in solvent-free mode, at relatively high temperature and pressure of CO_2 and in the presence of homogeneous and heterogenized catalysts. Different homogeneous i.e., quaternary ammonium salt halides and heterogeneous catalysts i.e., SiO_2-based grafted catalysts were tested. Very precise kinetic studies were conducted with the best catalyst by varying the reaction temperature (80-140 °C), CO_2 pressure (20-50 bar), catalyst loading (1.5-10 wt%) and stirring rate (400-800 rpm). The reaction products were purified with column chromatography and identified by ^{1}H- and ^{13}C-NMR as well as by GC-MS. The purified reaction products were utilized as standards for the calibration of the gas chromatographic (GC) method. The limonene diepoxide conversion and the products yields were analyzed with GC (DB-5 60m 0.32 mm column, and flame ionization detector). The solubilities of CO_2 in LDO and LDC were measured at different temperatures and pressures and the gas-liquid mass transfer coefficients were estimated with MATLAB software. Finally, density and viscosity of the reaction mixture were measured as a function of temperature and time of reaction.

Results and Discussion

The systematic kinetic experiments were conducted with tetrabutylammonium chloride (TBAC) as the catalyst, being the most active among the ones screened. The carbonation of LDO with CO_2 follows a consecutive mechanism through the formation of a monocarbonate intermediate (LC), as displayed in Figure 1.1, being in agreement with the study of Mikšovsky et al.[2]. As shown in Figure 1.2, complete conversion of LDO was reached after five hours at the highest reaction temperature and it increases with temperature. The yield of the intermediate LC over time has a maximum while the yield of the dicarbonate product LDC has an inflection point, which are both more pronounced at higher temperatures. As revealed by the kinetic experiments, the reaction temperature and the catalyst amount had a strong influence on both the reactant conversion and the product yields. Varying the CO_2 pressure, it was observed that the two consecutive reactions had a different dependence respect to the CO_2 concentration. Namely, the first reaction showed a zero reaction order with respect to CO_2 while the second one a first reaction order. This behavior can be explained by the variation of the solubility of CO_2 in the reaction media, which is higher at the beginning to then decrease. As a matter of fact, both the pressure and the temperature influenced the absorption of CO_2 in pure LDO and in the reaction mixture at 50% and 100% conversion of LDO. In particular, it decreased by increasing the conversion of LDO and the temperature of the system and increased by increasing the pressure of CO_2. The limonene dicarbonate was successfully separated from the reaction mixture by crystallization and subsequently fully characterized by NMR, IR and DSC.

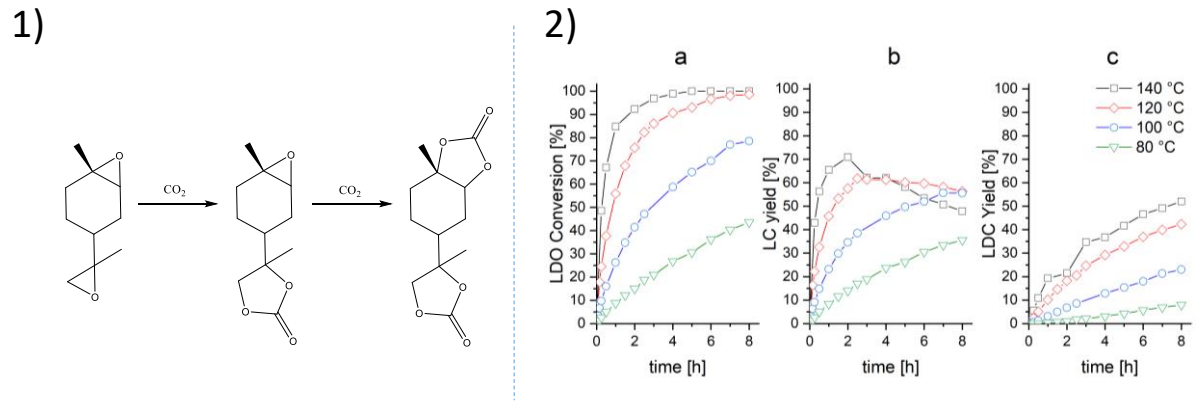


Figure 1. Reaction scheme of limonene dioxide carbonation (1). Temperature effect on the kinetics of CO_2 cycloaddition of limonene diepoxide (2).

References

1. A. Mija, E. Louisy, S. Lachegur, V. Khodyrieva, P. Martinaux, S. Olivero, V. Michelet, Green Chem., 2021, 23, 9855.
2. P. Mikšovsky, E. Horn, S. Naghdi, D. Eder, M. Schnurch, K. Bica-Schröder, Org. Process Res. Dev., 2022, 26, 10, 2799–2810

Acknowledgements

This study was carried out within the MICS (Made in Italy–Circular and Sustainable) Extended Partnership and received funding from the European Union Next-Generation EU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) – MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.3 –D.D. 1551.11-10-2022, PE00000004). This work is part of the activities financed by the Academy of Finland through the Academy Professor grants 319002, 320115, 345053 (Tapio Salmi, Federica Orabona). Economic support from Åbo Akademi University Graduate School (Federica Orabona) is gratefully acknowledged.

Low-content Ru catalysts for efficient atmospheric CO_2 methanation

Andrea Rizzetto, Marco Pietro Mezzapesa, Enrico Sartoretti,
Fabio Salomone, Marco Piumetti, Raffaele Pirone, Samir Bensaid*
Politecnico di Torino, Department of Applied Science and Technology (DISAT),
Corso Duca degli Abruzzi 24, 10129, Turin, Italy.
**samir.bensaid@polito.it*

Significance and Relevance

Ruthenium is regarded as a particularly active noble metal in the methanation reaction, exhibiting a low tendency towards deactivation and strong performance even at low loadings (1%-5%)[1], unlike nickel, which requires a higher loading (~20%). However, the high cost of ruthenium presents challenges to the large-scale development of Ru-based catalysts. Thus, this study aims to investigate the performance of catalysts with ultra-low Ru content (0.25%) during CO_2 methanation at atmospheric pressure. The objectives include comparing supports with varying redox properties to identify the optimal Ru-support combination, thereby maximising activity and stability, and minimising costs in potential industrial applications.

Preferred and 2nd choice for the topic: CO_2 utilisation and recycling / sustainable and clean energy production and transport
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The urgent need to reduce atmospheric CO_2, deepened by growing energy demands amid the energy crisis, has intensified research efforts to develop effective strategies for mitigating greenhouse gas emissions while generating value-added products[2,3]. A promising technology to address these challenges is the power-to-gas (PtG) process, which converts surplus electricity into H_2 via electrolysis, followed by the catalytic methanation of CO_2 in the gas phase[4]. This study investigates low-content Ru catalysts on various supports (Al_2O_3, CeO_2, TiO_2, MgO, ZrO_2), exploring the influence of low Ru loading on catalytic activity and metal-support interactions. Long-term stability tests and CO_2 conversion kinetics studies were conducted to assess catalyst durability and performance.

Materials and Methods

Ru-based catalysts were prepared by employing a water solution of ruthenium (III) nitrosyl nitrate (1.5 % w/w Ru) to impregnate dropwise commercial supports, namely γ-Al_2O_3, CeO_2, TiO_2, MgO, and ZrO_2 samples. These materials were dried at 120 °C for 4 h, calcined at 500 °C for 5 h in air, and reduced with 5 vol% H_2 in N_2 at 350 °C for 40 min. The nominal Ru loading was 0.25 wt% for all the catalysts. Time-on-stream (TOS) tests were conducted with a stoichiometric H_2/CO_2 ratio of 4 at 250 °C for three hours, while activity tests were performed across a temperature range of 200 to 400 °C under the same H_2/CO_2 ratio. Following these initial evaluations, the most effective catalyst was subjected to extended TOS testing (20 - 100 h) to assess its long-term stability and resilience rigorously. This comprehensive approach identified optimal operating conditions and provided insights into the catalyst's sustained performance under realistic process conditions. The morphological and physicochemical properties of the catalysts were thoroughly evaluated using a suite of complementary characterisation techniques, including H_2-TPR, CO_2-TPD, CO chemisorption, N_2 physisorption, XRD, and FESEM.

Results and Discussion

Despite the low Ru loading (0.25% Ru), all the catalysts demonstrated activity for atmospheric methanation, with varying degrees of effectiveness. Catalytic results (**Table 1**) revealed a light-off temperature from 200 to 250 °C under atmospheric pressure for four samples. Ru/TiO_2 exhibited the highest activity, achieving a CO_2 conversion of 21.2% and CH_4 selectivity of 99.8%, with the highest TOF (1.60×10^{-1} s^{-1}) at 250 °C. These results are likely attributed to strong metal-support interactions, high

catalytic activity of ruthenium species, facilitated by the support's high CO_2 adsorption capacity (186 $\mu mol_{CO_2}\ g^{-1}$). Ru/CeO_2 also showed high activity, with a conversion of 11.3% and a comparable TOF of $1.08 \times 10^{-1}\ s^{-1}$, again attributable to a good metal-support interaction (enhanced by ceria's redox properties) and a high catalytic activity of ruthenium species. In contrast, Ru/ZrO_2 and Ru/Al_2O_3 demonstrated lower conversions (7.6% and 6.8%, respectively) and similar TOFs ($8.40 \times 10^{-2}\ s^{-1}$ and $8.73 \times 10^{-2}\ s^{-1}$), and Ru dispersions of 42% and 35%, respectively. Weaker Ru-support interaction contributed to the lower performance of these two catalysts. Ru/MgO displayed the lowest conversion (0.5%) and TOF ($3.46 \times 10^{-3}\ s^{-1}$), despite its high basicity (891 $\mu mol_{CO_2}\ g^{-1}$). This suggests that the excessive basicity of the support and poor Ru reactivity negatively affected the results of this catalyst. When comparing the performance of the TiO_2-supported catalyst to that of the conventional Al_2O_3-supported system, Ru/TiO_2 demonstrated a CO_2 conversion threefold higher than that achieved by Ru/Al_2O_3 (21.2% against 6.8%), thereby underscoring its markedly superior catalytic activity. Furthermore, Ru/TiO_2 exhibited a TOF nearly twice that of Ru/Al_2O_3, reflecting a significantly enhanced reactivity of Ru active sites. Both catalysts exhibited high CH_4 selectivity; however, Ru/TiO_2 (99.8%) marginally surpassed Ru/Al_2O_3 (98.8%), indicating the advantageous interplay between the active metal and the TiO_2 support. These findings underscore the importance of balancing support basicity, Ru dispersion and metal-support interaction to optimise catalytic activity for atmospheric methanation.

Table 1. Catalytic performance and main physicochemical properties of the investigated catalysts

Samples	Conversion at 250 °C (%)	Selectivity to CH_4 (%)	CO_2 – TPD ($\mu mol_{CO_2}\ g^{-1}$)	TOF at 250 °C (s^{-1})	%D(1)	S_{BET} ($m_2\ g^{-1}$)
0.25% Ru/MgO	0.5	23.0	891	3.46×10^{-3}	18%	99.2
0.25% Ru/Al_2O_3	6.8	98.8	40.6	8.73×10^{-2}	35%	200
0.25% Ru/ZrO_2	7.6	99.0	21.3	8.40×10^{-2}	42%	4.4
0.25% Ru/CeO_2	11.3	96.3	16.4	1.08×10^{-1}	50%	11.5
0.25% Ru/TiO_2	21.2	99.8	186	1.60×10^{-1}	59%	45.7

(1) Metal dispersion of Ru particles estimated from selective chemisorption of CO at room temperature. Ru loadings are based on the nominal values.

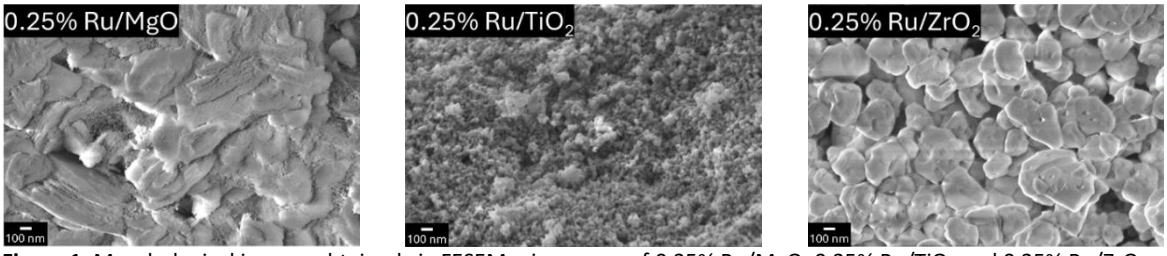


Figure 1. Morphological images obtained via FESEM microscopy of 0.25% Ru/MgO, 0.25% Ru/TiO_2 and 0.25% Ru/ZrO_2.

References

1 A. Rizzetto, E. Sartoretti, M. Piumetti, R. Pirone and S. Bensaid, *Chem. Eng. J.*, **2024**, 501, 157585.
2 A. Rizzetto, M. Piumetti, R. Pirone, E. Sartoretti and S. Bensaid, *Cat. Today*, **2024**, 429, 114478.
3 M. P. Mezzapesa, F. Salomone, H. Guzmán, F. Zammillo, R. Millini, L. Bua, G. Marra, A. Tacca, R. Marrazzo, N. Russo, R. Pirone, S. Hernandez and S. Bensaid, *Inorg. Chem. Front.*, **2024**, 11, 2319–2338.
4 F. Salomone, E. Giglio, D. Ferrero, M. Santarelli, R. Pirone and S. Bensaid, *Chemical Engineering Journal*, **2019**, 377, 120233.

Acknowledgements

The authors kindly thank METHA (Synthesis of renewable METHAne from CO_2 with advanced and robust catalysts) project funded by Compagnia di San Paolo through Bando "TRAPEZIO – Paving the way to research excellence and talent attraction" Linea 1: sostenere la ricerca competitiva. Enrico Sartoretti and Fabio Salomone acknowledge the Italian Ministry of University and Research (MUR), program FSE REACT-EU PON Ricerca e Innovazione (D.M. 1062/2021).

Deciphering Effects of Nanoparticles Shape and Size on the Structure Sensitivity of the CO_2 Methanation Reaction on Ni

Gabriele SPANO',[1‡] Matteo FERRI,[1‡] Raffaele CHEULA,[1] Matteo MONAI,[2]
Bert M. WECKHUYSEN,[2] Matteo MAESTRI[1*]

[1]*Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, Via La Masa, 34, 20156, Milano, Italy.*
[2]*Inorganic Chemistry and Catalysis Group, Institute for Circular and Sustainable Chemistry and Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands*.
‡These authors equally contributed to this work
**matteo.maestri@polimi.it*

Significance and Relevance

This work presents theoretical underpinnings that elucidate the nature of the high-debated structure sensitivity in CO_2 methanation over Ni, thus offering a framework that reconciles discrepancies in the experimental literature. By combining density functional theory with Boltzmann statistics, we capture the full diversity of Ni nanoparticle shapes under reaction conditions, revealing that shape, not just size, governs the overall catalytic performance. Our findings provide rational explanation to the different experimentally observed trends in the turnover frequency. Therefore, these insights can be applied to other structure-sensitive reactions, positioning this study as essential for advancing catalyst engineering and renewable energy solutions.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling; Multiscale modeling and advanced simulation aspects.
Preferred presentation: *Oral preferred or short oral*

Introduction and Motivations

Nickel nanoparticles are key catalysts for CO_2 methanation, a promising solution for renewable energy storage. For this reaction, the trend of turnover frequency (TOF) with Ni nanoparticle size remains debated. Some studies observe a maximum activity around 2.5 nm[1], while others report an increase of TOF with size, ultimately reaching a plateau[2]. This inconsistency highlights a lack of consensus regarding the origin of structure sensitivity for CO_2 methanation over Ni. Traditional particle models based on Wulff construction fail to explain these variations, as they rigidly provide only the equilibrium shape for each size. Thus, they overlook the diversity of nanoparticle shapes that can coexist for a given size under reaction conditions. To overcome these limitations, we employ the methodology proposed by Cheula et al.,[3] which allows to capture all the possible particle shapes for each size which exhibit a significant probability of occurrence. Our results reveal that TOF trends depend strongly on nanoparticle shape, not just size. The shape, in turn, can be affected by catalyst preparation method or choice of support material. Thus, we provide rational explanation to the different trends observed in the turnover frequency and offer critical insights for optimizing catalyst design.

Materials and Methods

DFT calculations are performed using the Quantum Espresso suite with the PBE functional. The nanoparticle ensemble, spanning sizes from 0.8 to 6.5 nm, is generated using the procedure from Cheula et al.,[3] based on cleaving bulk Ni into nanoparticles with various surface combinations. With a surrogate atomistic model, we compute the formation energy, and with a Boltzmann distribution we evaluate the probability of nanoparticle occurrence based on energy. Ni(111) and Ni(100) are found to be the most abundant facets of catalyst nanoparticles. Therefore, we adopt the microkinetic model proposed by Sterk et al.,[4] thus considering HCO^* dissociation into CH^* and O^* and $CH_3{}^*$ formation from

CH_2^* and H^* as rate determining steps over Ni(111) and Ni(100) respectively. In addition, we explicitly account for dissociation reactions that occur at the edge between these two facets.

Results and Discussion

As shown in Fig.1a, we obtain a TOF trend in excellent agreement with the experiments of Vogt et al.,[1] with a maximum activity around 2.5 nm. The overall activity is mainly attributable to the edge fraction of Ni(100) sites, since the active sites at the Ni(100)-Ni(111) interface are found to have the highest activity. However, particularly in proximity of the maximum between 1-3 nm, there is a broad distribution of particles whose activity significantly deviate from the average TOF trend. Indeed, multiple particle shapes coexist at the same size. Therefore, we divide Ni nanoparticles into families based on their shape, i.e., classifying them based on the fraction of Ni(100) sites, which spans in the range between 4-17%. Thus, we separately analyze the TOFs of the different Ni nanoparticles families. As shown in Fig1.b, particles with a high fraction of Ni(100) sites present a maximum in the activity around 2.2 nm. As the Ni(100) fraction decreases, the TOF flattens ultimately exhibiting a "hockey stick" behavior. These results show that the TOF trends are significantly different and depend strongly on the specific shapes of nanoparticle families. Therefore, this work highlights the critical need to consider both size and shape of catalyst nanoparticles to fully understand structure sensitivity of CO_2 methanation. The shape, in turn, can be affected by catalyst preparation method or the choice of support material. Operating conditions favoring particles with a high Ni(100) fraction lead to a maximum in the TOF with particle size. Differently, conditions promoting particles with a low Ni(100)-fraction results in a final plateau of the TOF, thus highlighting that shape, not just size, governs the overall catalytic performance. More broadly, these insights provide an explanation to the different trends experimentally observed in the turnover frequency and thus pave the way to study other structure-sensitive reactions, such as ammonia synthesis and decomposition.

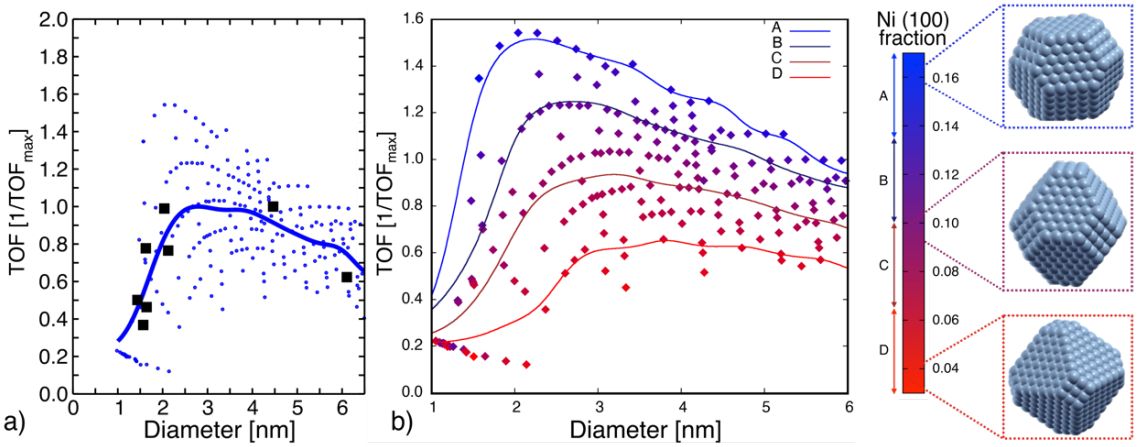


Figure 1. **(a)** TOF of the high-probability metal nanoparticles (dots) and filtered with a gaussian smearing (solid line) as a function of the diameter; experimental data of Vogt et al.[1] are reported as black squares. **(b)** TOF of the high-probability metal nanoparticles as a function of the diameter (dots), represented in terms of the Ni(100) sites fraction, according to the color bar. The lines represent a gaussian smoothing of four different families of metal nanoparticles, having similar Ni(100) fraction. Three selected metal nanoparticles with similar size (2 nm) and different shape (high, intermediate and low Ni(100) fraction) are reported in the insights of the color bar.

References

1. C. Vogt et al., *Nat. Catal* **2018**, *1*, 127-134.
2. N.L. Visser et al., *ChemCatChem*. **2022**, *14*.
3. R. Cheula et al., *ACS catalysis* **2020**, *8*, 3493-3503.
4. E.B. Sterk et al., *JACS Au* **2022**, *2*, 2714-2730.

Acknowledgements

Project funded under the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2, Investment 1.3, NextGenerationEU, Project NEST, PE0000021.

Enhancing CO_2ER to ethylene over CuO electrodes by Ni and B modification

Paolo Squillaci*, G. Papanikolaou, P. Lanzafame, D. Chillè, S. Perathoner and G. Centi
Department of Chemical, Biological, Pharmaceutical and Environmental Sciences (ChiBioFarAm) – University of Messina, ERIC aisbl and CASPE/INSTM, V.le F. Stagno d'Alcontres 31, 98166 Messina, Italy.
**paolo.squillaci@studenti.unime.it*

Significance and Relevance

The synergistic effects of Ni and B doping on CuO-based catalysts for CO_2 electroreduction (CO_2ER) were investigated. The results reveal that even at low concentrations, Ni significantly enhances the production of both CO and C_2H_4. Notably, the combined B-Ni modification of CuO demonstrated a pronounced synergistic effect, leading to a substantial increase in ethylene production, a suppression of the hydrogen evolution reaction (HER), improved current density, and enhanced catalyst stability. These findings highlight the potential of multi-level modifications to significantly improve catalyst activity, selectivity, and overall performance for CO_2ER applications.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling - Catalysis to electrify chemical production
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The CO_2ER presents a promising approach to transform CO_2 into valuable chemicals and fuels, such as ethylene, offering solutions to both environmental and energy challenges[1]. However, the selectivity of Cu-based electrodes and their long-term stability at high current densities remain significant challenges. To address these issues, this work investigated the synergistic effect of Ni and B as doping agents on a CuO-based catalyst in the production of ethylene through CO_2ER. Ni was selected for its excellent capacity to produce CO, while B was chosen for its ability to dimerize CO, facilitating the production of C_2H_4[2,3].

Materials and Methods

CuO-based catalyst was synthesized by adding a solution of sodium hydroxide to a copper nitrate aqueous solution. Subsequentially, a suitable amount of nickel nitrate and boric acid was added in the solution, under stirring. Finally, the solution was heated at 373K for 12h into a capped Teflon-lined autoclave. The catalysts obtained were designated as CuONS (nanosheets) for the pristine catalyst, Ni_1CuONS for the catalyst modified with Ni, and B_1Ni_1CuONS for the catalyst modified with both Ni and B. The amount of modifier was set at 1%wt. Scanning Electron Microscope (SEM-EDX), Inductively coupled plasma-optical emission spectroscopy (ICP-OES), X-Ray Diffraction (XRD), Linear Sweep Voltammetry (LSV), Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) were employed for characterization. The electrocatalytic tests were conducted at different applied potential (-0.8V, -1V and -1.2V vs RHE) in a gas/liquid phase FlowCell (FC) operating in a three-electrode configuration where the working electrode is a catalyst-based gas diffusion electrode (GDE) with a 10cm^2 active area.

Results and Discussion

SEM images reveal that all catalysts exhibit a nanosheets morphology. Following modification with B and Ni, the predominant nanosheet morphology is retained; however, the nanosheets become more agglomerated when Ni is added during the synthesis. ICP-OES and EDX analysis revealed that the Ni content is 0.6 wt%, while B is present at trace levels below 0.05 wt%. The presence of the CuO phase in all catalysts was confirmed by XRD. Additionally, the catalyst modified with Ni exhibited a new peak corresponding to the presence of NiOOH. The electrocatalytic behavior was investigated through LSV, revealing a progressive increase in current at the same potential after modification with Ni and B, compared to the pristine CuONS. This improvement is attributed to the lower charge transfer

resistance (R_{ct}), as determined by EIS, for the modified-CuO catalysts. Moreover, the CV in the non-faradaic region was used to determine the double-layer capacitance (CdL) and, consequently, the Electrochemically Active Surface Area (ECSA). The results revealed that after Ni and B modification, an increase in the ECSA value of pristine CuONS occurred, reaching a higher value for the B and Ni co-modified catalyst.

The electrocatalytic activity of the catalysts was studied through a chronoamperometry (CA) test in a three-electrode FC in an alkaline environment (1 M KOH). As shown in Figure 1, the pristine CuONS exhibited good selectivity toward C_2H_4, which slightly increased after the introduction of Ni into the structure. Moreover, an increase in CO production and a decrease in HER were observed at all applied potentials due to the presence of Ni. After the co-modification of pristine CuONS with Ni and B, an increase in current density was observed, attributed to the higher ECSA value and lower R_{ct}, reaching 140 mA/cm² at -1.2 V (vs. RHE) due to the presence of B. The co-modified CuONS reached a FE toward C_2H_4 of 61% at the same applied potential. Finally, the B_1Ni_1CuONS catalyst was tested for 10 hours under the same conditions, demonstrating good stability and consistent ethylene production, with a maximum FE toward ethylene of 63% and a minimum of 58% at the end of the test.

These results highlight how the synergistic effects of Ni, which selectively favors CO production and suppresses HER, combined with the benefits of B, which boosts current density and promotes CO dimerization, can be utilized to enhance ethylene production at industrial-level.

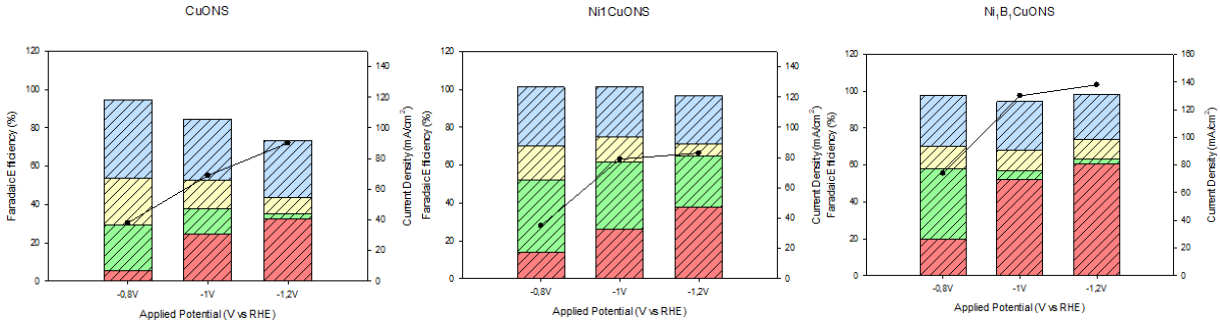


Figure 1. *Current density and Faradaic efficiency (FE) at different applied potentials for all catalysts. The Faradaic efficiencies for C_2H_4, CO, HCOOH, and H_2 are represented by red, green, yellow, and blue colors, respectively.*

References

1. G. Papanikolaou, G. Centi, S. Perathoner, P. Lanzafame, *Chinese J. Catal.* 2022, 43(5), 1194–1203.
2. L. Huang, Z. Liu, G. Gao, C. Chen, Y. Xue, J. Zhao, Q. Lei, M. Jin, C. Zhu, Y. Han, J. S. Francisco, X. Lu, *J. Am. Chem. Soc.* 2023, 145, 48, 26444–26451.
3. Q. Wan, J. Zhang, B. Zhang, D. Tan, L. Yao, L. Zheng, F. Zhang, L. Liu, X. Chenga, B. Han, *Green Chem.*, 2020,22, 2750-2754.

Acknowledgements

Paolo Squillaci thanks the Ministry of University and Research (MUR) for the grant received in the frame of the project D.M. 352 co-financed Versalis S.p.A (CUP J94D22000730009).

Effect of zeolite acidity on pre-treated Fe-based catalysts for e-fuel production via CO_2-modified Fischer-Tropsch Synthesis

Alessio TAURO[1], Fabio SALOMONE[*,1], Fabrizio CELORIA[1], Luca NODARI[2], Luca ROMAGNOLETTI[3], Emanuele FELLI[4], Raffaele PIRONE[1], Samir BENSAID[1]

[1] *Polytechnic of Turin, Dept. of Applied Science and Technology, Corso Duca degli Abruzzi 24, 10129 Turin, Italy.*
[2] *Istituto di Chimica della Materia Condensata e di Tecnologie per l'Energia (ICMATE), Consiglio Nazionale delle Ricerche (CNR), C.so Stati Uniti 4, 35127 Padova, Italy.*
[3] *API Raffineria di Ancona S.p.A., Via Flaminia 685, 60015 Falconara Marittima (AN), Italy.*
[4] *Italiana Petroli S.p.A., Via Salaria 1322, 00138 Roma, Italy.*
** fabio.salomone@polito.it*

Significance and Relevance

This work is significant in advancing CO_2-modified Fischer-Tropsch synthesis (FTS) by exploring the role of zeolite acidity in influencing Na-Fe_3O_4 catalyst selectivity and product distribution. By combining extensive characterization techniques, including Detailed Hydrocarbon Analysis (DHA) and Mössbauer spectroscopy, with chemometric tools like Principal Component Analysis (PCA), the study provides a comprehensive understanding of how catalyst phase composition and zeolite choice impact hydrocarbon profiles. These insights are essential for developing tailored catalysts that optimize CO_2-to-hydrocarbon conversion, promoting sustainable fuel production.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling / Sustainable and clean energy production and transport
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The increasing demand for sustainable fuels has accelerated research in CO_2 conversion technologies, particularly in the Fischer-Tropsch synthesis (FTS) process for generating liquid hydrocarbons. This study investigates the impact of zeolites with different acidities on a Na-Fe_3O_4 catalyst in CO_2-modified FTS. Specifically, the research explores how different zeolites can enhance the conversion efficiency and selectivity of the catalyst, offering new insights into optimizing the CO_2-to-hydrocarbon pathway.

Materials and Methods

The Na-Fe_3O_4 catalyst was synthesized and combined with commercial zeolites, then subjected to optimized pre-treatment conditions based on prior work [1]. Catalyst and product characterizations were performed using XRD, Mössbauer spectroscopy, and Detailed Hydrocarbon Analysis (DHA), to examine bulk composition, surface properties, and hydrocarbon distributions. Principal Component Analysis (PCA) was applied to the DHA data to reveal correlations between molecular compositions and test conditions, highlighting how different zeolites influence hydrocarbon profiles.

Results and Discussion

Two pretreatment methods were evaluated: H_2 activation (pretreatment A) and H_2 activation followed by carburization (CO/H_2) at 400°C (pretreatment AC400). The H_2 activation facilitated the formation of Hägg carbide (χ-Fe_5C_2), producing hydrocarbons mainly in the gasoline range. In contrast, the AC400 pretreatment promoted the formation of ε'-$Fe_{2.2}C$, a more active phase selective for longer-chain hydrocarbons[2]. Both pretreatments were combined with four MFI zeolites with increasing acidity (SiO_2/Al_2O_3 ratios of 23, 38, 80, and 117). The addition of zeolites shifted the oil product distribution from olefin/naphthene-rich to iso-paraffin/aromatic-dominant compositions (Fig. 1) and increased the C6+ yield by at least 25%[3]. DHA identified and quantified over 150 hydrocarbons, clarifying how zeolite acidity influences reaction mechanisms. Chemometric analysis, particularly PCA, identified recurring

patterns in hydrocarbon formation associated with different SiO_2/Al_2O_3 ratios. Mössbauer spectroscopy further clarified the zeolites' influence, showing changes in both product distribution and phase transformations during FTS. This study demonstrates the importance of integrating multiple characterization techniques, including detailed analysis of both liquid products and catalyst structures, to provide a comprehensive understanding of CO_2-modified FTS. The synergistic use of DHA, PCA, and Mössbauer spectroscopy offers a novel and thorough approach for optimizing catalysts and reaction pathways in sustainable fuel production.

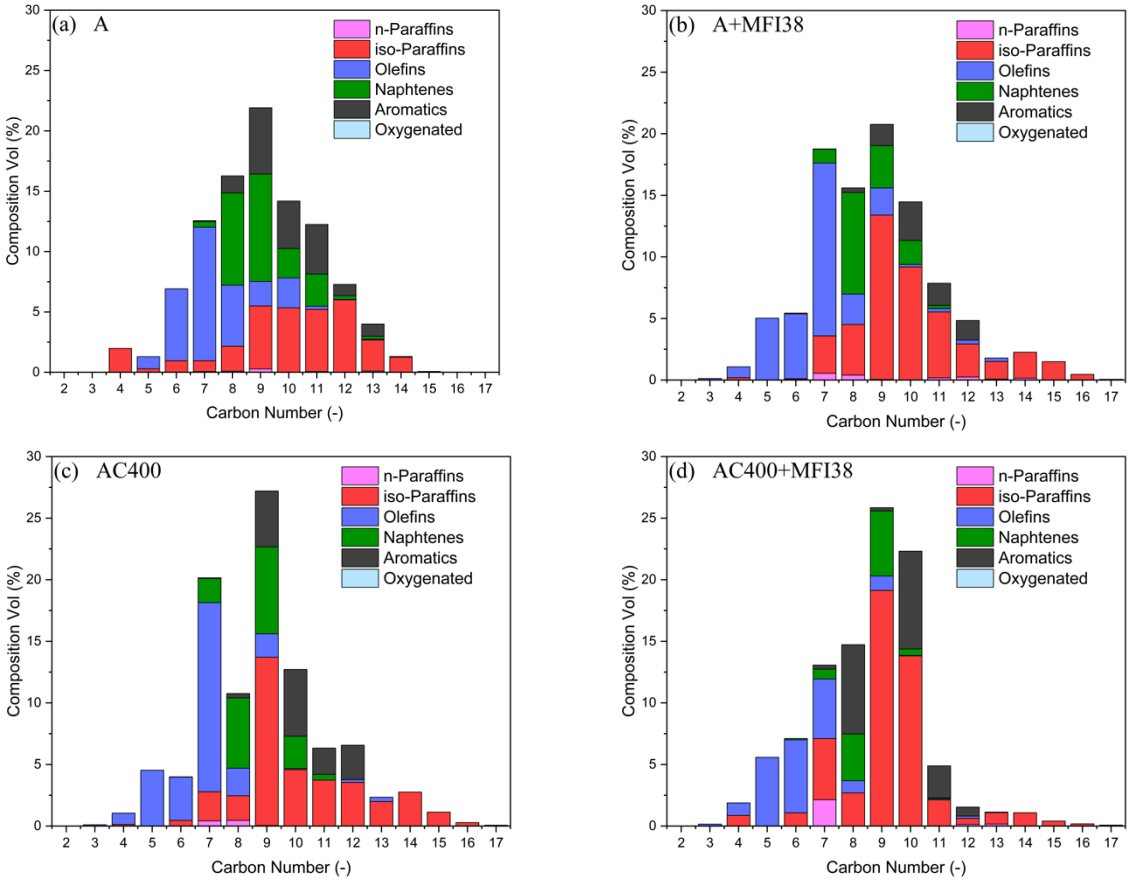


Figure 1 Detailed Hydrocarbon Analysis profiles for samples pretreated with H_2 activation alone (a), H_2 activation coupled with MFI38 (b), H_2 activation followed by 400°C carburization alone (c), and H_2 activation with 400°C carburization coupled with MFI38 (d).

References

1. M. V. Landau, N. Meiri, et al., Ind Eng Chem Res **2017**, vol. 56, no. 45, pp. 13334–13355
2. F. Lu, X. Chen, et al., Appl Catal B **2021**, vol. 281, p. 119521
3. E. Corrao, F. Salomone, et al., Cheml Eng Res and Des **2023**, vol. 197, pp. 449–465

Acknowledgements

The authors acknowledge the project PON Ricerca e Innovazione "REACT-EU" (DM 1062/21) funded by the Italian MUR and the PNRR program (DM 352/22) funded by the "Next Generation EU" program of the EU. Thanks to the Department of Chemical Sciences of Università di Padova for the Mössbauer analysis. Thanks to the API Raffineria di Ancona, Falconcara Marittima (Ancona) for the liquid samples analysis.

Promoted Fe catalyst for direct conversion of CO_2 into *e-crude*

Mattia Piacentini[1], Beda Rolandi[1], Alessandro Porta[1], Luca Lietti[1], Carlo Giorgio Visconti[1]*
[1]*Laboratory of Catalysis and Catalytic Processes, Department of Energy*
Politecnico di Milano, via La Masa 34, 20156, Milano ITALY
* carlo.visconti@polimi.it

Significance and Relevance

A promoted iron-based catalyst was tested under conditions favoring high selectivity to *e-crude*, primarily in the C_8-C_{16} range, with CH_4 and C_2-C_4 paraffins accounting for less than 15%. The catalyst showed a reversible deactivation, mainly driven by water partial pressure.

Preferred and 2nd choice for the topic: CO_2 Utilization and Recycling
Preferred presentation: Oral and short oral preferred

Introduction and Motivations

Developing a direct process to convert CO_2 into long-chain hydrocarbons via modified Fischer-Tropsch (MFT) is highly promising for producing sustainable e-fuels for high energy density applications (e.g. aviation fuels). MFT produces a wide range of products, distributed across gas and condensed phases. The condensate phase, referred to as *e-crude*, contains a mixture of high energy density hydrocarbons, making it ideal for applications like aviation where energy density is essential. However, MFT catalysts are susceptible to deactivation due to oxidation of iron carbides, the active phase for the chain growth of the Fischer-Tropsch [1]. In this work, a promoted iron-based catalyst was tested in conditions to achieve a high selectivity to *e-crude*, with minimal production of CH_4 and lower paraffins. Despite a long exposure to a high partial pressure of water caused evolving performances during time on stream, the catalyst showed reversible deactivation.

Materials and Methods

Following the procedure reported in [2], a co-precipitated Fe-Zn oxide was promoted by incipient wetness impregnation with potassium carbonate and copper nitrate. The final catalyst composition was 100Fe:10Zn:1Cu:4K on a molar basis.
High pressure catalytic tests have been carried out in a fixed bed stainless steel (AISI 316 L) reactor with an internal diameter of 1.1 cm, located inside an electrical tubular oven. The effluent gases exiting the reactor were sent firstly to a hot trap kept at 120 °C to remove heavier hydrocarbons (up to C_{35}) and then to a cold trap kept at 2 °C, to remove the lighter fraction and water. Incondensable gases leaving the vessels were periodically analyzed by an on-line GC. Prior to the reaction the catalyst was activated in-situ with syngas (H_2/CO= 2 mol/mol) at 270 °C for 1h at atmospheric pressure.

Results and Discussion

The catalyst was tested for more than 900 hours on stream, investigating different operating conditions. The catalyst reaches pseudo steady state after about one day on stream, showing high selectivity to C_{5+} and low selectivity to light hydrogenated compounds (CH_4 and lower paraffins) in most of the investigated conditions. Interestingly, CO_2 conversion is higher than the thermodynamic equilibrium of the sole RWGS reaction. The ratio between the RWGS reaction quotient and the equilibrium constant (Kp_{RWGS}/Keq_{RWGS}) is always between 0.7 and 1, suggesting that the RWGS is close to its equilibrium. Thus, the consecutive FT converts CO into hydrocarbons, removing the product of the RWGS from the reaction environment increasing the overall conversion. Stability check points (colored areas in Fig 1) show that catalyst performances evolve over time. For example, comparing areas “B” and “D”, CO_2 conversion decreases significantly from 33% to 23%, together with an increase in CO selectivity from 14% to 35%. Consequently, selectivity to C_{5+} drops from 51% to 29%. This deactivation is attributed to H_2O partial pressure. Indeed, at 30 barg and 350°C the partial pressure of H_2O reaches 8 barg (area “C” in Fig 1), leading to iron carbide oxidation to iron oxide and reduced FT activity. The sample was regenerated at

350°C and 5 barg (area “E” in Fig 1) where low partial pressure of H_2O and high partial pressure of CO restored most of the carbide phase and FT catalytic activity. The yellow area “F” in Fig 1 shows that, after the regeneration, the catalyst's performance is restored to levels comparable to area "B". Figure 2 shows the complete product distribution obtained at 300 °C, 30 barg and 6 L(STP)/h/gcat (area “A” Fig 1). The product distribution closely follows a bimodal Anderson-Schultz-Flory (ASF) model, with a change in slope at C_{15}. The product pool consists primarily of linear olefins, but also includes branched hydrocarbons, linear paraffins and a non-negligible amount of alcohols. Notably, about 60% of the produced *e-crude* is within the C_8-C_{16} range, making it particularly suited for aviation fuels applications.

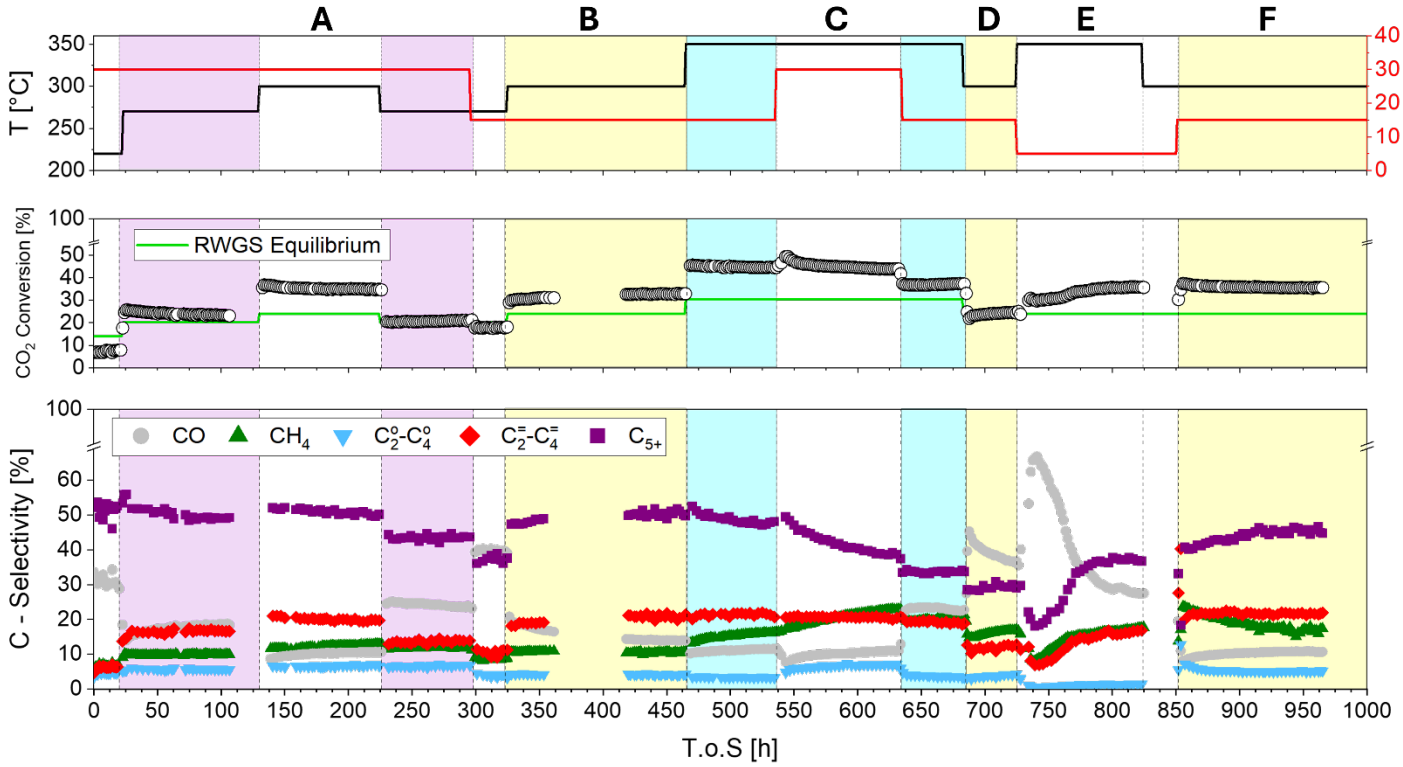


Figure 1. From top: Operative conditions, CO_2 Conversion and product selectivity as function of ToS. All data are obtained at 6 L(STP)/h/gcat.

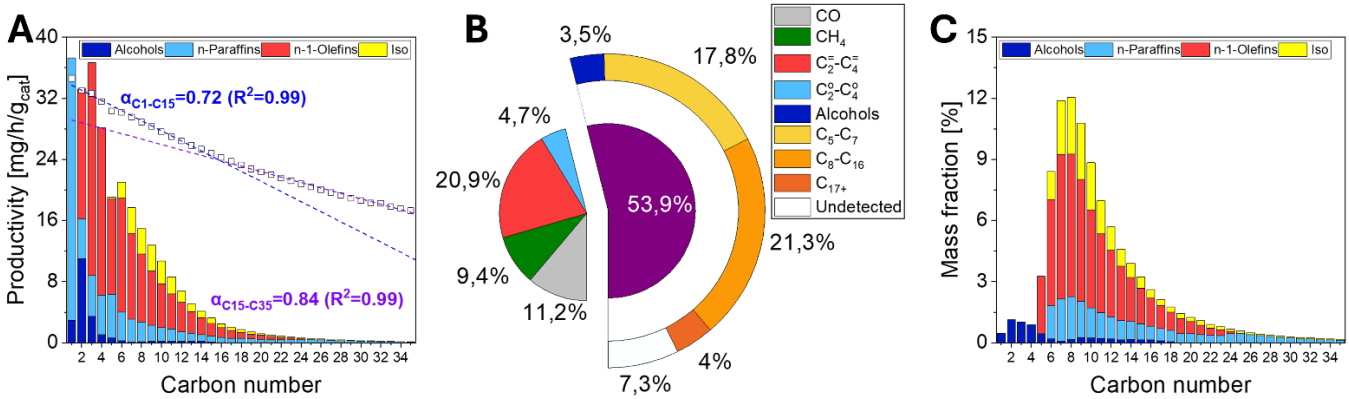


Figure 2. A) Complete product distribution and ASF plot B) Complete carbon-based selectivity C) *e-crude* characterization. Operating conditions: 300 °C, 30 barg and 6 L(STP)/h/gcat.

References

1. Ramos et al., Appl. Catal. B 2024, 347, 123794
2. M. Martinelli et al., Catalysis Today 2014, 228, 77

Effective upgrade of CO_2 and CH_4 to high-value products over iron-containing Al-rich *BEA zeolite

Kinga MLEKODAJ[1], Kinga GORA-MAREK[*,2], Karolina TARACH[2], Julia Sobalska [2,3], Agnieszka KORNAS[1], Radim PILAR[1], Dalibor KAUCKY[1], Edyta TABOR[*,1] …….

[1] *J. Heyrovský Institute of Physical Chemistry of the CAS, v. v. i., Dolejškova 2155/3, 182 23 Prague 8, Czech Republic.*

[2] *Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Kraków, Poland.*

[3] *Doctoral School of Exact and Natural Sciences, Jagiellonian University in Krakow, Łojasiewicza 11, 30-348 Krakow, Poland.*

** kinga.gora-marek@uj.edu.pl, and edyta.tabor@jh-inst.cas.cz*

Significance and Relevance

The chemical recycling of CO_2 and CH_4 into platform chemicals has attracted considerable attention from industry and academia. Here, we demonstrate the direct and efficient conversion of these waste gases into acetic acid, with methyl acetate as a secondary product (both achieving 35% efficiency), using iron active centres in an Al-rich *BEA zeolite catalyst. The selected zeolitic matrix enhances reagent transport, while tailored synthesis achieves a high aluminum concentration, ensuring a substantial fraction of iron active species. Together, these factors deliver exceptional catalytic activity for the direct processing of CO_2 and CH_4 into valuable chemical products.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling / Fundamental advances in understanding catalysis

Preferred presentation: Oral only / Oral preferred

Introduction and Motivations

Converting CO_2 and CH_4 into platform chemicals provides a sustainable way to utilize these abundant greenhouse gases, mitigating their environmental impact while reducing reliance on fossil feedstocks. This approach supports the transition to a circular carbon economy by transforming waste emissions into valuable chemical intermediates for industrial applications. CO_2 or CH_4 molecules can be effectively activated over transition metal ion-containing (TMI) zeolites as catalysts.[1-2] TMI centres in zeolites exhibit unique electron-donating properties that can lower the energetic barrier for C-H bond cleavage and possess intrinsic acidity, facilitating the transfer of Brønsted acid protons. These two characteristics enable the formation of critical reaction intermediates, their subsequent conversion, and the efficient desorption of desired products.[3-5] For this study, we selected a wide-pore zeolite with *BEA topology, focusing specifically on a sample with a low Si/Al molar ratio to maximize its capacity to host TMI centers. The Al-rich *BEA zeolite was synthesized using a template-free approach to minimize the environmental impact typically associated with zeolite production. The aim was to harness the catalytic potential of iron species, known for their high activity in redox processes.

Materials and Methods

For our study, we utilized laboratory-synthesized Al-rich *BEA zeolite (Si/Al = 4.5), characterized by a high concentration of aluminum pairs capable of stabilizing divalent iron ions. After synthesis, the zeolitic material underwent structural characterization by XRD. The state of Al atoms was analysed using ^{27}Al and ^{29}Si MAS NMR. The distribution of Al atoms in the synthesized sample was determined using a well-established, multi-spectroscopic method based on the analysis of its Co-form[6]. The sample was converted to its NH_4-form and subsequently impregnated with a solution of $FeCl_3$ in acetylacetonate to obtained three Fe-*BEA samples with Fe/Al varying between 0.06-0.3. Iron speciation in such prepared samples was characterized using FTIR, Mössbauer, UV-Vis, and XAS spectroscopies. The activity of iron centres embedded in Al-rich *BEA zeolite for CO_2 and CH_4 utilization was monitored using operando FTIR-MS. Prior to the catalytic process, the samples were dehydrated under a dynamic vacuum at 450 °C. Following this, a mixture of CO_2 and CH_4 in an equimolar ratio was introduced into the system. The reaction was studied over a temperature range of 250–450 °C.

Results and Discussion

The template-free synthesis of Al-rich *BEA zeolite yielded a sample with a Si/Al ratio of 4.5, exhibiting diffraction patterns characteristic of zeolites with this topology. NMR studies confirmed that all Al atoms are exclusively located in the tetrahedral positions of the framework. Analysis of Al atoms revealed that 30% of the Al atoms can stabilize divalent iron species. The introduction of iron produced materials with Fe/Al ratios ranging from 0.06 to 0.3. Spectroscopic analysis revealed the exclusive presence of bare Fe(II) in samples with Fe/Al ratios < 0.15. However, as the Fe loading increased, iron oxo mono- and binuclear species were observed. Iron oxide was also detected in the sample with the highest Fe/Al ratio, in addition to bare cations and iron oxo species. Hyperfine parameters obtained from Mössbauer spectroscopy of dehydrated Fe-*BEA samples, combined with pre-edge features from XAS spectra, confirmed that all studied samples contained a fraction of bare divalent iron cations, which are predominantly located within six-membered rings of the zeolitic framework. The presence of Fe(II) species in Al-rich Fe-*BEA was confirmed by FTIR analysis using CO as a probe molecule. The interaction of the studied iron-containing zeolites with CO resulted in the appearance of a new band in the FTIR spectrum around 2190 cm^{-1}, indicating the formation of a Fe(II)CO monocarbonyl complex. The interaction of equimolar CO_2 and CH_4 with Fe-*BEA zeolites was monitored in-situ by FTIR across a temperature range from RT to 300°C. The FTIR results confirmed the emergence of new bands in the region of 1750–1300 cm^{-1}, typical for CH_3, CHO, and COO^- groups. Additionally, a decrease in the intensity of bands corresponding to CH_4 and CO_2 was observed. The temperature range of 200–300°C was selected for catalytic testing due to the formation of high-intensity bands in the FTIR spectrum originating from acetic acid. Activity tests revealed signals with m/z values of 60 and 74 in the mass spectra (Figure 1) of reactor exhaust gases following the interaction of dehydrated Fe-*BEA samples with an equimolar CO_2 and CH_4 mixture. These signals, attributed to acetic acid and methyl acetate respectively, appeared at temperatures above 230 °C, with maximum concentrations observed at 450 °C. The catalytic efficiency for producing these products was 35%. In the catalytic process, both Fe(II) and easily reducible Fe(III) species played active roles. The presence of CH_4 reduced iron-oxo species, thereby integrating them into redox cycles. The results presented here offer an efficient and straightforward approach for processing CO_2 and CH_4 at low temperatures into value-added products.

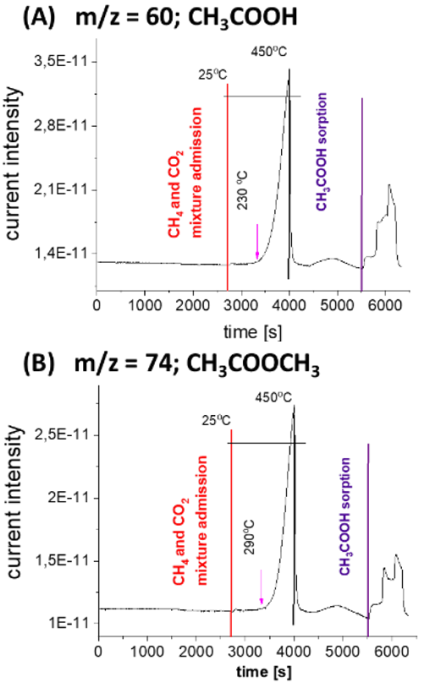


Figure 1 Activity of Al-rich Fe-*BEA in direct transformation of carbon dioxide and methane into acetic acid (A) and methyl acetate (B).

References

1. Q. Zhang, J. H. Yu and A. Corma, Adv. Mater., **2020**, 32, 2002927.
2. M. Zabilskiy, V. L. Sushkevich, M. A. Newton and J. A. van Bokhoven, ACS Catal., **2020**, 10, 14240.
3. C. Tu, X. Nie and J. G. Chen, ACS Catal., **2021**, 11, 3384.
4. G. Zhao, M. Drewery, J. Mackie, T. Oliver, E. M. Kennedy and M. Stockenhuber, Energy Technol., **2020**, 8, 1900665.
5. W. Zhou, K. Cheng, J. C. Kang, C. Zhou, V. Subramanian, Q. H. Zhang, Y. Wang, Chem. Soc. Rev., **2019**, 48, 3193.
6. J. Dedecek, E. Tabor, S. Sklenak, ChemSusChem, **2019**, 12, 556.

Acknowledgements

The authors thank the Czech Science Foundation #24-14387L and the National Science Centre, Poland, 2022/47/I/ST4/00607 for the financial support.

Electrification by Induction Heating for Sustainable Dehydrogenation of Ethylbenzene to Styrene

Ahmed Ragab Saleh Belmashkan,[1] Gianfranco Giorgianni[1], Vahideh Abbassi[1], Siglinda Perathoner[1], Gabriele Centi[1], Angelo Ferrando[2], Gianni Marchetti[2], Salvatore Abate[1]*

[1] *Department of ChiBioFarAm (Industrial Chemistry), University of Messina, ERIC aisbl and INSTM/CASPE, V.le F. Stagno d'Alcontres 31, Messina 98166, Italy*
[2] *Basic Chemical & Plastics Research Centre Versalis - Stabilimento di Mantova Via Taliercio 14, 46100 Mantova, Italy*

** abates@unime.it*

Significance and Relevance

The electrification of chemical processes leverages renewable electricity to power chemical reactions and operate processing equipment, offering a pathway to enhanced energy efficiency and sustainability in the chemical industry. Among the emerging technologies, induction heating presents a promising alternative, particularly for the dehydrogenation of ethylbenzene to styrene. [1] This method offers several advantages, including reduced energy consumption, minimized safety hazards, and precise control over the heating zone. By enabling localized heating, ensures that the reaction ceases as soon as the reagent exits the heated zone, effectively preventing the formation of unwanted byproducts.

Introduction and Motivations

The dehydrogenation of ethylbenzene to styrene is a critical reaction in the production of plastics, a key component in various industrial applications. However, conventional methods for this process demand high temperatures and excessive use of superheated vapor, which contribute to significant environmental risks such as increased greenhouse gas emissions and high energy demands.

This study focuses on the feasibility of employing ferrite nanoparticle core-shell catalysts in combination with induction heating for the dehydrogenation of ethylbenzene to styrene. The research aims to evaluate the potential industrial and environmental advantages of this novel approach by directly comparing it to the performance of commercial catalysts used in current industrial processes.

The aim of this work is to develop a core-shell catalyst structure, where the core is made of ferrite, and the shell consists of silica. Additional active phases, as potassium (K) and cerium (Ce) are incorporated using various methods. Through this comparison, the study seeks to provide a comprehensive understanding of the efficiency, scalability, and environmental impact of adopting this method.

Materials and Methods

The synthesis of the catalyst involves two main procedures: the preparation of the core-shell structure and the incorporation of active phases.

Fe_3O_4@SiO_2 nanoparticles were synthesized via a sol-gel method. By using commercial Fe_3O_4, tetraethyl orthosilicate (TEOS), deionized water, ethanol and ammonium hydroxide. [2]

The second procedure involved the addition of active phases, specifically (K and Ce). The catalysts were characterized using various physic-chemical techniques, including TGA, XRD, XPS, TEM, and BET analysis.

The amount of catalyst used for testing is 0.12 g with the feed mixture is 0.7% Vol of EB in N_2 (10mL/min) for 3 hours. A reduction treatment is exclusively performed on the commercial catalyst at 600 °C in pure H_2 for one hour.

Results and Discussion

The prepared catalysts were assessed in an uninsulated quartz fixed bed reactor using magnetic induction heating. The measured (via pyrometer) surface temperature was 400°C; the internal temperature remains undetermined, and can arguably achieve the material Curie temperature, i.e. 550°C. For the sake of comparison, a commercial catalyst was subjected to conventional heating at 550°C.

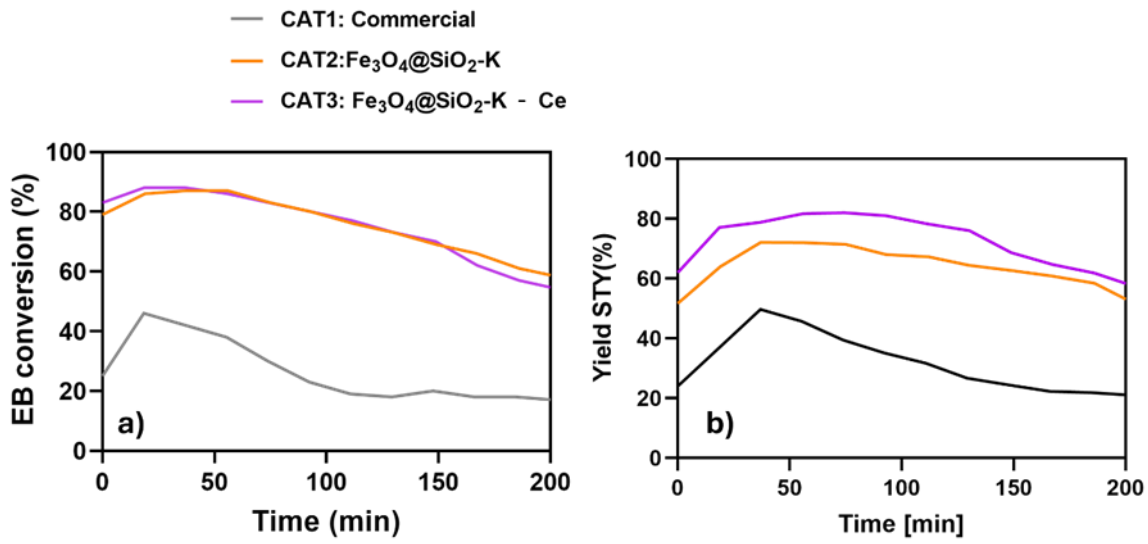


Figure 1 - Performance comparison of ethylbenzene (EB) dehydrogenation catalysts in terms of (left) EB conversion and (right) yield of styrene (STY).

All catalysts initially exhibited high ethylbenzene (EB) conversion, which gradually decreased probably due to coke formation and deposition on the catalyst surface. The data demonstrate that induction heating enables high conversion rates compared to conventional heating at the investigated operation conditions.

Figure 1 illustrates that the incorporation of active phases such as K and Ce, into the core-shell Fe_3O_4@SiO_2 catalyst led to progressively improved performance compared to the commercial catalyst. Notably, the Fe_3O_4@SiO_2 catalyst modified with K (CAT2) achieved an initial conversion rate of approximately 85%, which declined to about 60% after 200 minutes. The inclusion of Ce (CAT3) followed a similar trend in terms of conversion but notably enhanced the yield towards styrene (STY), effectively reducing coke formation and extending catalyst activity.

In summary, these core-shell catalysts, when heated via magnetic induction, operate effectively and provide improved performance, with sustained conversion rates and low byproduct formation. Hence, potential energy costs reduction and environmental impact minimization look promising; catalyst internal temperature and total energy consumption shall be investigated.

References

1. Højlund Nielsen, Paul Erik; Nielsen; Hansen, J. B. T. M. (2017). Dehydrogenation Of Ethylbenzene to Styrene (Patent No. WO 2017/072059 A1).
2. Chae, H. S., Kim, S. D., Piao, S. H., & Choi, H. J. (2016). Core-shell structured Fe_3O_4@SiO_2 nanoparticles fabricated by sol–gel method and their magnetorheology. *Colloid and Polymer Science*, *294*(4), 647–655.

Acknowledgements

This work was supported by the ERC Grant “Surface-Confined Fast Modulated Plasma for Process and Energy Intensification" (SCOPE), Grant No. 810182

Modification of Ordered Mesoporous Carbon materials for Enhancing the Electrocatalytic Oxidation of Phenol to p-benzoquinone

Donatella CHILLÉ*, Paolo SQUILLACI, Georgia PAPANIKOLAOU, Siglinda PERATHONER, Gabriele CENTI and Paola LANZAFAME

Department of Chemical, Biological, Pharmaceutical and Environmental Sciences (ChiBioFarAm), University of Messina, ERIC a.i.s.b.l. and CASPE/INSTM, V.le F. Stagno d'Alcontres 31, 98166 Messina, Italy

** dchille@unime.it*

Significance and Relevance

Selective electrocatalytic oxidation (ECO) offers a promising and sustainable strategy for valorizing phenolic compounds, the primary constituents of lignin biomass. ECO of phenols was mainly studied by employing catalysts based on critical raw materials or heavy metals and oriented to the total mineralization of the organic molecule. This study paves the way to the valorization of a lignin-derived molecule, since phenol is selectively converted to p-benzoquinone, by exploiting available materials such as ordered mesoporous carbons, properly modified by the incorporation of phosphorous as heteroatom. The well-defined structure of these materials should ensure a short transport way for ions and electrons and the presence of the heteroatom, modifying the electron distribution of the carbon network, could improve the electrochemical behaviour.

Preferred and 2nd choice for the topic:
1) Advanced process with electrocatalysis and plasma utilization
2) Green chemistry and biomass transformation, renewable resources conversion
Preferred presentation: Short oral/poster

Introduction and Motivations

Phenolic compounds, the fundamental building blocks of lignin, the second most abundant component of lignocellulose, are considered toxic compounds often found in industrial effluents such as from pulp and paper, plastics, pharmaceutical, pesticide, oil and petrochemical industries. Thus, they represent a hazard for living organism especially for their refractory and, for this reason, most of the last investigations have been addressed to the total degradation.[1] This study explores the valorization of phenol through electrocatalytic oxidation using phosphorus-modified ordered mesoporous carbons free of critical raw materials, selectively producing p-benzoquinone, a compound with several applications.[2] Furthermore, the influence of metal oxides, such as NiO, on selectivity was also examined.

Materials and Methods

Ordered Mesoporous Carbon (OMC) was synthesized using Santa Barbara Silica (SBA-15) as template and glycerol as carbon source. The polymer-template composite was pyrolyzed under nitrogen flow and the silica template was removed by HF treatment. The OMC was then properly modified by introducing phosphorous by following the hard templating method in which 2,7-dihydroxynaphthalene was employed as carbon source while tris(4-methoxyphenyl)phosphine as heteroatom precursor for producing POMC. The deposition of NiO on POMC (NiO@POMC) was performed by wet impregnation and all the resulting materials were analyzed through chemical and structural characterization.

Gas Diffusion Electrode (GDE), used as working electrode, was prepared by depositing by airbrush an ink containing an appropriate amount of the catalyst powder, Nafion® solution (binder) and ethanol onto a Gas Diffusion Layer (GDL).

Chronoamperometric measurements were conducted in a micro FlowCell in a three-electrode configuration by employing 0.1M phosphate buffer solutions at different pH= containing 100mg/L of phenol. Products identification was performed by High Performance Liquid Chromatography (HPLC) and by Gas Chromatography (Micro GC).

Results and Discussion

The XRD showed the characteristic peaks of carbon at 2θ=24° and 2θ=43°of 002 and 100 diffraction planes, typical of graphitic materials. After doping, a slight shift towards lower angles of the 002 crystal plane was registered, pointing out the incorporation of phosphorous in the OMC structure. The diffraction pattern of NiO@POMC reported the typical diffraction peaks of the metal oxide, highlighting that NiO was successfully incorporated in the POMC catalyst. Cyclic voltammetries evidenced that each catalyst is active in the anodic oxidation of phenol to p-benzoquinone, showing in the 1st anodic scan the characteristic peak of phenol oxidation followed, from the 2nd anodic scan, by the formation of another anodic peak ascribable to the oxidation of phenol to p-benzoquinone.

Chronoamperometric tests revealed that phenol conversion increased following the introduction of phosphorous on OMC. A further enhancement in the electrocatalytic perfomances was observed after the deposition of NiO on POMC, which yielded a conversion approaching 60% and a selectivity towards p-benzoquinone of approximately 50%.

This research presents a sustainable and efficient electrocatalytic method for phenol oxidation to p-benzoquinone using heteroatom-doped OMCs. The incorporation of phosphorous and NiO results in a substantial improvement in catalytic performance, attributed to enhanced hydrophilicity, electrical conductivity and the presence of large amount active sites introduced by heteroatom doping and metal centers. Therefore, these results could pave the way for the use of CRM-free carbon materials as anodes for the electrocatalytic valorization of lignin-derived molecules.

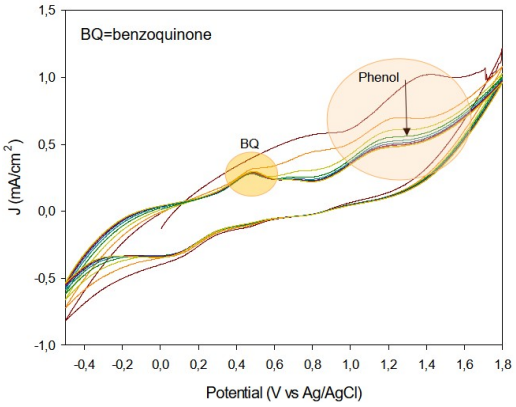


Figure 1. Consecutive cyclic voltammetry scans of NiO@POMC recorded at 10mV/s in 0.1M phosphate buffer solution at pH=3 containing 100mg/L of phenol.

References

1. H. Yapeng et al., *Separation and Purification Technology*. 2019, 212, 802–821
2. O.T. Can, M. Bayrmoglu, *Journal of Hazardous Materials.* 2010, 173, 731-736

Acknowledgements

This work was realized in the frame of the activities of the EU project *EPOCH* (*Electrocatalytic Production of liquid Organic hydrogen carrier and CHemicals from lignin*; No 101070976)

Unveiling the deactivation process of Amberlyst-15 in the etherification reaction of glycerol with ethanol

Mario SAMPERI[1], Giuseppe BONURA[1], Mariarita SANTORO[1], Serena TODARO[1], Alessandro CAJUMI[2], Mauro FAILLA[1], Francesco ARENA[2], Catia CANNILLA[1]
[1]*Institute of Advanced Technology for Energy CNR-ITAE, S. Lucia sopra Contesse 5, 98126 Messina, Italy. Institution, Dept., address, city, country.*
[2]*University of Messina, Dept. of Engineering, c.da Papardo, 98166 Messina, Italy.*
**mario.samperi@itae.cnr.it*

Significance and Relevance

This work discloses the operating limits and the critical aspects associated with the use of Amberlyst-15 as heterogeneous catalyst for the etherification of glycerol with ethanol to oxygenated additives for biodiesel. Although this strongly acidic resin is widely recognized in the literature as an effective catalyst for this reaction, its lifetime and stability has been generally overlooked. Our findings demonstrate that although elevated temperatures (≅200°C) enhance conversion and yield to *poly*-ethers, A significant deactivation occurs after the first catalytic run. An in-depth physicochemical characterization of the used catalyst provides valuable insights into the deactivation process.

Fundamental advances in understanding catalysis
Oral preferred or Short Oral

Introduction and Motivations

Biofuels are increasingly recognized as an important renewable energy source, particularly for their potential in reducing greenhouse gas emissions and dependence on fossil fuels. The valorization of glycerol, the main by-product of biodiesel production, has emerged as a significant area of research to enhance biofuel quality, efficiency and environmental sustainability[1]. One promising approach is the etherification reaction, through which glycerol can be converted into oxygenated poly-substituted ethers. These compounds improve combustion properties, enhance fuel stability, lower viscosity, and facilitate blending with petroleum diesel. The glycerol etherification reaction involves the use of various *O*-alkylating agents, such as alkenes or alcohols, in the presence of solid catalysts like sulfonic resins or acidic zeolites[2]. The choice of catalysts and reactants significantly affects the efficiency, selectivity, and yield of glycerol ethers, as well as the overall cost of large-scale production[3]. This study explores the etherification of glycerol using ethanol, a widely available and cost-effective alcohol, to promote sustainability in biofuel production. However, the use of primary alcohols presents a notable challenge due to the more stringent reaction conditions required for their activation.

Materials and Methods

The etherification of glycerol with ethanol was carried out in a stainless-steel batch reactor under autogenous pressure in inert atmosphere. The products and catalyst were easily separated by filtration and then analyzed. The etherification reaction was carried out within a temperature range of 140–220 °C, varying the reaction time (R_t) from 1 to 24 hours, the ethanol-glycerol molar ratio ($R_{EtOH/Gly}$) ranging from 4:1 to 15:1, and the catalyst amount between 3 and 30 wt.% with respect to glycerol. The reaction mixture was analyzed offline by gas chromatography (GC), while compounds identification was carried out by GC–Mass analysis. A detailed catalyst characterization of both fresh and spent catalysts was performed by hyphenated thermogravimetric analysis-mass spectroscopy (TGA-MS). Finally, X-ray photoelectron spectroscopy (XPS) was employed for additional structural investigation.

Results and Discussion

Glycerol conversion, selectivity and yield of *di*- and *tri*-ethers (DEGs and TEG) are strongly dependent on temperature and reaction time. At low temperatures, glycerol conversion (χ_{Gly}) varies significantly with the reaction time, while selectivity and yield of DEGs/TEG values result to be similar.

On the other hand, irrespective of the reaction time, high temperatures have a minor influence on glycerol conversion, whereas selectivity and yield are significantly affected. The most relevant results were obtained at 220°C after 24h, with a glycerol conversion of 88.7% and DEGs/TEG yield of 46.8%. However, these experimental conditions deeply affect the catalyst stability. The activity is quite low at 140°C (χ_{Gly}=12.3%), but the catalyst remains stable over five catalytic runs, whereas at 180°C, the remarkable activity recorded after the first run (χ_{Gly}=56.9%) is followed by an abrupt catalyst deactivation. TGA/MS analyses carried out on both fresh and used catalyst were useful to obtain important information on the structure of Amberlyst-15 and to define the main reasons behind the loss of catalytic activity. Specifically, the thermal stability of the fresh catalyst at 180°C indicates that the reason behind its deactivation after the reaction is to be found on the chemical modification of the active sites. TGA/MS measurements allowed observing the presence of both physisorbed and chemisorbed products on the catalyst surface, whose formation is driven by temperature (Figure 1A). This evidence has been confirmed by XPS measurements (Figure 1B), which highlight a complex *sulfur* structure consisting of sulfonic and sulfynil groups, together with disulfide bonds on the backbone of the polymeric structure. On the whole, the characterizations on used catalysts suggest the occurrence of a covalent bond involving sulfonic groups and the reaction products, which represents the main path of deactivation.

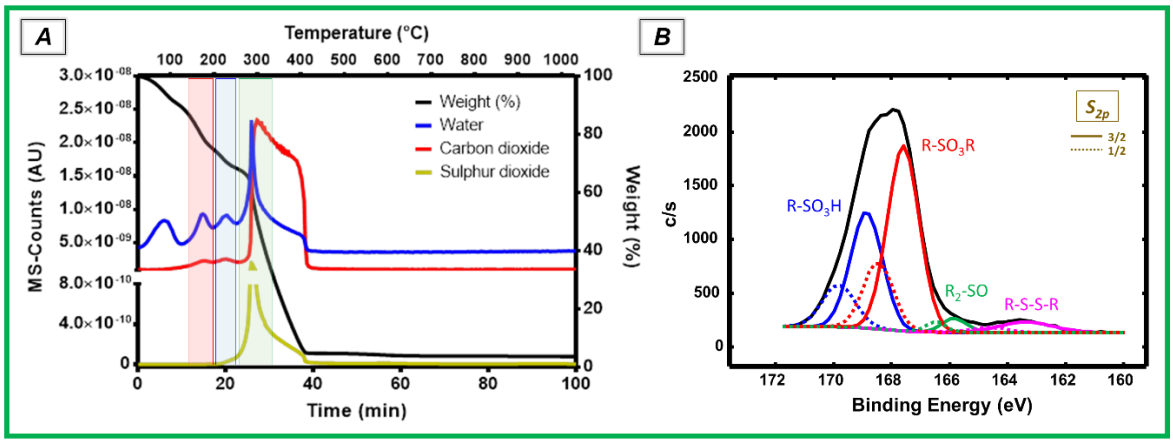


Figure 1 (A) TGA/MS of used Amberlyst-15 at 160°C (1 run). XPS spectrum S_{2p} of Amberlyst-15 used at 180°C (1 run). (B) Experimental conditions: $R_{EtOH/Gly}$=9 mol/mol, R_t=6h, Amberlyst-15=10%wt to glycerol.

References

1. N. Yadav, G. Yadav, M. Ahmaruzzaman, *Industrial Crops and Products* **2024**, *210*, 117999.
2. C. Cannilla, G. Bonura, S. Maisano, L. Frusteri, M. Migliori, G. Giordano, S. Todaro, F. Frusteri, *Journal of Energy Chemistry* **2020**, *48*, 136-144.
3. C. Cannilla, G. Giacoppo, L. Frusteri, S. Todaro, G. Bonura, F. Frusteri, *Journal of Industrial and Engineering Chemistry* **2021**, *98*, 413-424.

Acknowledgements

This research was funded by the EU – NextGeneration EU from the Italian Ministry of Environment and Energy Security POR H2 AdP MMES/ENEA, the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.4 - Call for tender No. 3138 of December 16, 2021 of Italian Ministry of University and Research funded by the European Union – NextGeneration EU (CN-MOST-SP14).

Steel slag as a highly efficient catalyst for hydrodeoxygenation of fatty acids: from a residue to a precious material for renewable fuels production

Stefano SAVINO[1,*], Giuseppe GUGLIELMO[2], Rosella ATTROTTO[2], Elena GHEDINI[3], Michele CASIELLO[1], Fiorenza FANELLI[1], Lucia D'ACCOLTI[1,3], Angelo NACCI[1,3]

[1] *ICCOM-CNR, SS Bari, Via Orabona 4, 70126 Bari, Italy.*

[2] *Research and Development Department, Acciaierie d'Italia S.p.A., SS Appia km 648, 74123 Taranto, Italy.*

[3] *Chemistry Department, Università degli Studi di Bari Aldo Moro, 70125 Bari, Italy.*

** stefano.savino@iccom.cnr.it*

Significance and Relevance

Steel slag, the abundant and cheap residue of steel industry, was found to be an active and highly selective catalyst in the hydrodeoxygenation (HDO) of fatty acids. This material, not always recyclable, proved to function in the pristine state (without any chemical and thermal pre-treatment), truly promoting the hydrothermal conversion of palmitic and stearic acids into the corresponding alkanes (C16 and C18) with a selectivity higher than 90%.

Preferred and 2nd choice for the topic:

- *Green chemistry and biomass transformation, renewable resources conversion.*
- *Sustainable and clean energy production and transport*

Preferred presentation: Poster

Introduction and Motivations

The global transition towards sustainable energy and the need for reducing greenhouse gas emissions (GHG) have prompted extensive research into renewable fuels[1]. Among various biomass feedstocks, fatty acids (FAs) have attracted attention due to their abundant availability and potential for conversion into high-energy hydrocarbons[2]. One of the most promising methods for upgrading FAs is hydrodeoxygenation (HDO), a catalytic process that removes oxygen from long carbon chains of carboxylic acid functionalities. The HDO reaction of fatty acids generally requires harsh conditions (200-450 °C, under P_{H_2} in the range of 4-12 MPa), and either noble or non-noble metal catalysts, preferentially anchored on supports (zeolites, alumina, silica etc.) and assembled as sulfided, bimetallic, or alloy form[3].

In this context, very intriguing appears the use of steel slag, an abundant and cheap residue of steel industry that seems to be a candidate for large-scale applications. Although the steel slags are already recycled up to 80 %, their use is for the most as inert material in the civil sector[4]. However, by virtue of their composition rich in metals, a better way to exploit this material is to transform it into an efficient and recyclable catalyst[5].

Our previous studies have already shown that steel slag displays good catalytic properties in the energy field, promoting the CO_2 photoreduction to solar fuels[6,7] and the transesterification of triglycerides[8] to give FAMEs. In this context, we predicted that this residue of industry can become a precious HDO catalyst, thus widening the range of applications of this material to a catalytic field where it has never been employed.

Materials and Methods

Steel slag was provided by "Acciaierie d'Italia," the only Italian steel producer based on integrated steel production cycle (main plant located at Taranto, Italy). Reactions were conducted in a stainless-steel reactor monitoring pressure and temperature.

Results and Discussion

Hydrodeoxygenation conditions were chosen based on the results coming from a literature[9] survey. The experimental set-up has been calibrated to handle 100 - 500 mg of fatty acid, under a hydrogen pressure of 16 bar, using the largest grain slag available. From the preliminary experiments conducted

on two representative substrates, namely palmitic (PA) and stearic acid (SA), encouraging results have emerged, attested by a complete and highly selective conversion (>90%) of model fatty acids into the corresponding HDO products, hexadecane (C16) and octadecane (C18). Next, palmitic acid was selected as the substrate for carrying out further investigations, mainly aimed at studying the factors affecting the reaction course.

At first, the influence of substrate/slag amount ratio was monitored. The expected lower catalytic activity (due to the large granule sizes) was exploited to magnify the influence of such parameter as shown in Figure 1a. A very low conversion was observed with a substrate/slag ratio of 5:3, suggesting an inhibiting effect of the massive amounts of PA substrate adsorbed on the catalyst surface compared with the poor number of available active sites. By reversing the ratio in favor of the slag, conversions increased until reaching completeness with a 1:3 ratio. The blank experiment, conducted without the slag, confirmed that this material is truly a catalyst for the process.

The influence of the particle dimensions was deeply investigated using five different slag range sizes through proper grinding and sieving processes (steel slag as it is, and four fractions separated according to grain size). As expected, conversion increased with the decrease of the average granule dimensions, reaching an 80% of conversion with the smallest grains of slag (Fig. 1b). Temperature also affected HDO reaction in the predictable manner. To magnify the influence of such parameter a higher substrate/slag ratio (5:1 wt/wt) and the smallest slag sizes (210-90 µm) were used, monitoring a very large temperature range within 260 – 340 °C (Fig. 2c). Higher temperatures were avoided due to the growth of undesirable cracking side-products. Expectedly, the raise of temperature improved the slag performance in a sensible manner, allowing to reach a 60% of conversion without decreasing selectivity towards HDO product.

These investigations have preliminarily shown that steel slag, provides promising catalytic properties for the synthesis of green diesel. Steel slag was shown to be effective and especially selective in the process of deoxygenation, favoring the desired pathway of hydrodeoxygenation (HDO) and minimizing the parasitic processes of cracking, decarbonylation (DCN) and wax production.

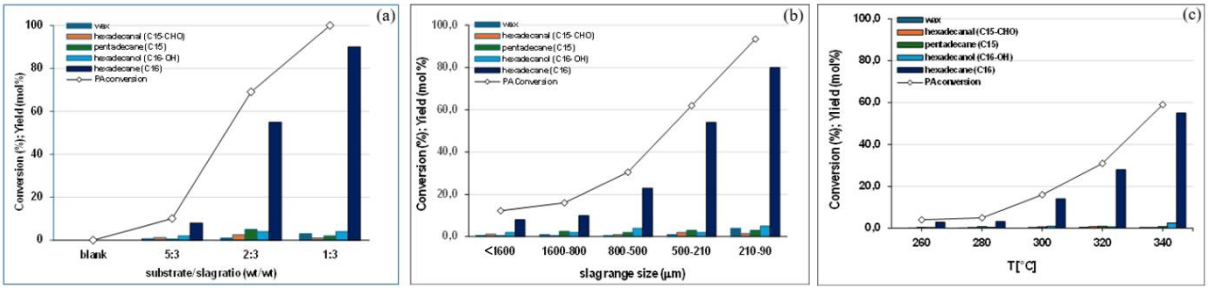


Figure 1 Studies of factors affecting HDO reaction.

References

1. Biomass Conversion and Biorefinery 2022, volume 14, Issue 7, Pages 8153 – 8188, https://doi.org/10.1007/s13399-022-03057-0.
2. International Journal of Green Energy Volume 21, Issue 11, Pages 2530 – 2550, 2024 https://doi.org/10.1080/15435075.2024.2319219.
3. Energies 2023, 16, 844. https://doi.org/10.3390/en16020844.
4. https://www.euroslag.com/.
5. M. Hamza, M. Ayoub, Environmental Technology & Innovation, 2021, 21, 101200, https://doi.org/10.1016/j.eti.2020.101200.
6. Scientific Reports | (2022) 12:11378 | https://doi.org/10.1038/s41598-022-15554-3.
7. Case Studies in Chemical and Environmental Engineering 11 (2025) 101050, https://doi.org/10.1016/j.cscee.2024.101050.
8. Catalysts 2021, 11, 619. https://doi.org/10.3390/catal11050619.
9. ChemCatChem 2017, 9, 195 – 203 https://doi.org/10.1002/cctc.201601162.

Oxidative dehydrogenation of ethane combined with CO_2 splitting *via* chemical looping technique utilising redox of In_2O_3

Kosuke WATANABE[1], Takuma HIGO[1], Koki SAEGUSA[1], Sakura MATSUMOTO[1], Hiroshi SAMPEI[1], Yuki ISONO[2], Akira SHIMOJUKU[2], Hideki FURUSAWA[2], and Yasushi SEKINE[1*]

[1]*Waseda University, Department of Applied Chemistry, Shinjuku, Tokyo 169-8555, Japan.*

[2]*JX Advanced Metals Corporation, Isohara Branch, Technology Develop Center, Kitaibaraki, Ibaraki 319-1535, Japan.*

**ysekine@waseda.jp*

Significance and Relevance

We developed a novel oxygen carrier $Ni_{1-x}Cu_x$-In_2O_3, which showed high reaction rates with high oxygen capacity in a chemical looping system, combining ethane oxidative dehydrogenation and CO_2 splitting at a low temperature of 873 K. This oxygen carrier releases and backfills oxygen through non-topotactic redox of In_2O_3 and the transformation of Ni-Cu and Ni-Cu-In alloy, and this unique mechanism achieves outstanding performance. This achievement contributes to efficient ethylene production and CO_2 utilisation and proposes a new strategy for chemical looping processes in general.

Preferred and 2nd choice for the topic: "Green chemistry and biomass transformation, renewable resources conversion", "CO2 utilization and recycling"
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Currently, ethylene production is responsible for 0.8% of global CO_2 emissions due to its huge demand and the high reaction temperature required (> 1123 K)[1]. Catalytic oxidative dehydrogenation of ethane is one promising alternative process because it proceeds at low temperatures, but the mixing of ethane and oxidants is causing difficulties in industrialisation. Applying chemical looping technology for oxidative dehydrogenation (CL-ODH) greatly increases its feasibility[2]. Employing materials with oxygen storage and release ability (oxygen carrier: OC) achieves oxidative dehydrogenation through two separate sub-steps: selective oxidation of ethane with lattice oxygen release from the OC, followed by lattice oxygen backfilling with oxidant. This system, which operates without gas mixing, addresses the challenges of gas separation, side reactions, and safety concerns associated with conventional oxidative dehydrogenation while also enabling higher equilibrium yields compared to direct dehydrogenation. Furthermore, simultaneous conversion to CO can be achieved if CO_2 can be used for OC regeneration.

In this study, we found that In_2O_3 modified with Ni-Cu alloy exhibited excellent performance in ethylene production and CO_2 splitting at a low temperature of 873 K. This presentation will discuss the unique reaction mechanism enabling this coupling of difficult reactions, as well as the roles of In, Ni, and Cu elements in the process.

Materials and Methods

All OCs were prepared by a complex polymerisation method. Activity evaluation was conducted in a fixed bed flow reactor at 873 K. In this test, 500 mg of OC was used, with an alternating supply of 50% C_2H_6 and 50% CO_2 (each at a total flow rate of 60 mL/min). In the performance comparison, the results are based on the analysis of the gas collected in a gas bag during the first 5 min of the 2nd cycle.

Results and Discussion

Based on structural analysis by XRD and STEM-EDX, it was found that $Ni_{1-x}Cu_x$-In_2O_3 starts with a structure in which In_2O_3 is modified with a Ni-Cu binary alloy, and then

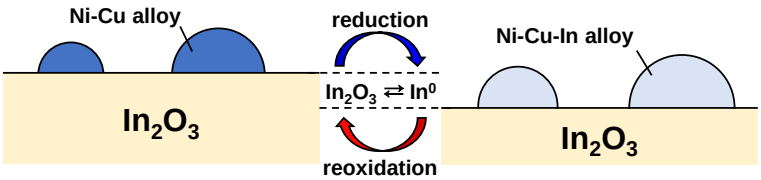


Figure 1 schematic image of redox of $Ni_{1-x}Cu_x$-In_2O_3.

forms a Ni-Cu-In ternary alloy by incorporating In^0, which is formed by the reduction of In_2O_3 by C_2H_6. In the regeneration process with CO_2, In^0 was oxidised and returned to a structure composed of Ni-Cu binary alloy and In_2O_3. The schematic image is shown in Figure 1.

C_2H_4 formation was evaluated at 873 K. Modification with Ni and/or Cu significantly enhanced activity compared to bare-In_2O_3. Among these, Ni-Cu alloy modification exhibited superior performance relative to either Ni or Cu alone. In particular, modification with Cu-rich alloys, such as $Ni_{0.1}Cu_{0.9}$, achieved both high activity and selectivity, with a trend toward decreased selectivity as the Ni content increased. $Ni_{0.1}Cu_{0.9}$-In_2O_3, which exhibited the best performance, was found to release and regenerate more than 4wt% of lattice oxygen, as determined by thermogravimetric analysis. The regeneration process involving CO_2 splitting was faster in Cu-rich OCs, and in $Ni_{0.1}Cu_{0.9}$-In_2O_3, it was completed in a similar time to the C_2H_6 oxidation process.

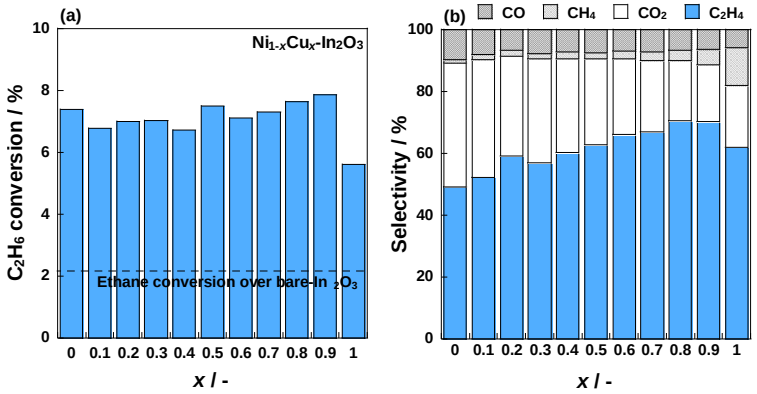


Figure 2 (a) C_2H_6 conversion and (b) products distribution during the ethane oxidation step over $Ni_{1-x}Cu_x$-In_2O_3.

The result of C_2H_6-TPR measurement showed that modification with Ni and/or Cu significantly improves the reduction of In_2O_3. Since Cu itself has a poor ability to activate C_2H_6; therefore, it is considered that Cu plays a role in facilitating access of the gas phase to the lattice oxygen of In_2O_3 by incorporating In^0 by alloying. There are two peaks in the region below 873 K in the TPR profile (peak 1 and peak 2 in Figure 3). Peak 1 attenuated as the Ni content decreased, and this was consistent with the trend in CO_2 selectivity during C_2H_6 supply. Therefore, peak 1 is considered to correspond to the decomposition of C_2H_6 over Ni ensemble and the combustion of products by the lattice oxygen of In_2O_3. $Ni_{0.1}Cu_{0.9}$-In_2O_3 exhibited superior activity and selectivity compared to Cu-In_2O_3, with the only difference in the TPR profile being the presence of peak 2, indicating that peak 2 contributes to the selective oxidation of C_2H_6. Detailed examination of the structural changes during the OC reduction process and evaluation of the activation barrier of C-H cleavage at each active site by theoretical calculation were conducted, and it is suggested that peak 2 corresponds to ethane dehydrogenation at Ni sites in the Cu-Ni-In ternary alloy formed during the reaction process and hydrogen combustion.

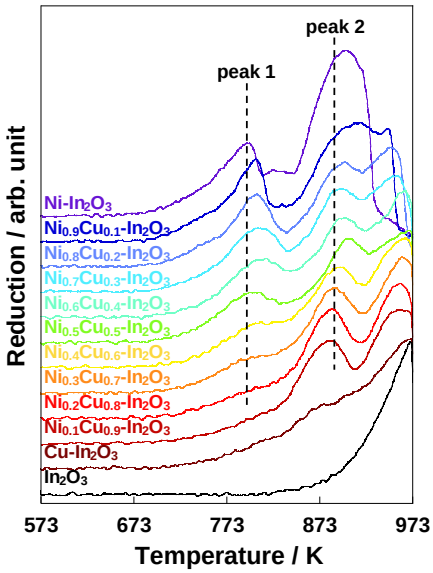


Figure 3 C_2H_6-TPR profiles of $Ni_{1-x}Cu_x$-In_2O_3.

In conclusion, the modification with Ni-Cu significantly improved the performance of In_2O_3 as an oxygen carrier. In the selective oxidation process of C_2H_6, In_2O_3 was reduced to In^0 and incorporated into the Ni-Cu alloy to form the ternary alloy. The incorporation of In^0 prevents In_2O_3 surfaces from being covered by In metal and assists in the reaction by releasing lattice oxygen of In_2O_3. Cu suppressed side reactions by breaking Ni ensemble and promoted the CO_2 splitting step. Ni promoted the activation of C_2H_6, and in particular, the Ni species in ternary alloy formed during the reaction showed higher activity.

References

1. A. H. Tullo, *c&en* **2021**, 99, 9.
2. Y. Gao, L. Neal, D. Ding, W. Wu, C. Baroi, A. M. Gaffney, and F. Li, *ACS Catal.* **2019**, 9, 8592–8621.

Structurally Controllable Strong Acid Mesoporous Catalyst SBA-15-TESBS: Synthesis and Application in Biodiesel Production

LIJIANG FAN [1], EIKA QIAN [1], KENJI KAMIYA [1], PENG MINGMING [1]

[1] : Tokyo University of Agriculture and Technology.

Corresponding author (EIKA QIAN). E-mail: whqian@cc.tuat.ac.jp

Significance and Relevance

By using 4-(Triethoxysilyl)benzenesulfonic acid (TESBS) as a silicon source instead of Tetraethyl orthosilicate (TEOS) in the synthesis of SBA-15, the amount of acid sites and catalytic activity in esterification, transesterification, and isomerization of palm acid oil can be significantly enhanced. When the TESBS ratio reached 30%, the acid content in the catalyst increased to 1.4 mmol/g, effectively improving its catalytic performance. This modification led to a remarkable enhancement in the low-temperature flowability of the resulting product. This study also investigates how the catalyst's structure and acidity change under varying synthesis conditions.

Primary topic:： *Green chemistry and biomass transformation, renewable resources conversion*
Secondary topic: Sustainable and clean energy production and transport
Preferred presentation: ORAL preferred or SHORT ORAL.

Introduction and Motivations

The refining of palm oil results in the production of a byproduct, palm acid oil (PAO), which contains triglycerides (TG <70%) and free fatty acids (FFA >30%) as waste products. In the past, this laboratory has developed a BDF production process using solid acid catalysts to react PAO with methanol. However, the poor low-temperature flowability of the BDF has proved problematic. This may result in fuel filter clogging and poor engine performance in cold climates [1]. To address these problems, studies have shown that isomerization of the product can improve its low-temperature flowability [2]. Research indicates that Brønsted acids have the capability to promote the isomerization of unsaturated fatty acids [3]. SBA-15, a mesoporous catalyst with a large surface area and high-temperature stability, offers significant advantages[4]. However, its low Brønsted acid content limits its effectiveness in skeletal isomerization. Therefore, this study aims to develop a sulfonic acid-modified SBA-15-MPSBS catalyst to enhance esterification, transesterification, and isomerization reactions, thereby addressing the challenge of poor low-temperature flowability in biodiesel fuel (BDF). Additionally, the study explores the structural and acidity variations of the catalyst under different synthesis conditions.

Materials and Methods

TESBS was introduced into SBA-15 surface to synthesize a mesoporous mesopore-SBA-15-benzene sulfonic acid (MPSBS). During the synthesis, TESBS/TEOS ratio, the removal method for P123, and reaction temperature etc. were investigated. The catalysts were characterized by use of BET, XRD, and Boehm acid-base back titration.

The reaction feedstock consisted of a model oil prepared by mixing erucic acid (FFA22:1) and triolein (TG18:1) in a 3:7 ratio. The experiments were conducted using a batch reactor, with a reaction temperature of 260°C and a reaction time of 3 hours. Additionally, the esterification, transesterification, and skeletal isomerization performance of the model compounds were evaluated. The products were analyzed using GC-FID and GC-MS. To assess the low-temperature flowability of the resulting oil, the slip point [5] was measured.

Results and Discussion

1. synthesis of SBA-15-MPSBS

Table 1 lists the results of the amount of acid in prepared SBA-15-MPSBS. With the increase of TESBS, the acid amount of the catalyst rises significantly. Due to TESBS being almost the sole source of acidity, it indicates that even with a TESBS content of up to 30%, TESBS can still be successfully incorporated onto the surface of SBA-15. The acid amount reached 1.4 mmol/g. It could be theorized that increasing the proportion of MPSBS will result in a continuous increase in the acid amount of the catalyst. However, it should be noted that the benzene ring structure of MPSBS will affect the size of

the original structure of SBA-15. XRD spectra showed that all catalysts successfully had the structure of SBA-15.

.2. Catalyst activity

In the experiment, a batch reactor was used, the reaction temperature at 220~260 °C for 3 hours. Experiments were conducted to investigate the effects of varying ratios of MPSBS (2% to 30%) on the observed activity. In accordance with the preceding findings, the proportion of MPSBS augmented, concomitant with an increase in the quantity of acid present within the catalyst. The results of the activity experiment are presented below. It can be concluded that an increase in the quantity of acid present in the catalyst results in a notable enhancement in the activity of the esterification, transesterification and isomerization reactions. Using SBA-15-MPSBS (30) at 260°C for 3 hours, the low-temperature flowability of the product is greatly improved.

Conclusion

By using TESBS instead of TEOS as the silicon source for SBA-15, a large amount of acidic substance can be successfully introduced, significantly enhancing the catalytic activity of SBA-15 while maintaining the integrity of its structure. Through the method developed in this study successfully produces BDF with excellent low temperature flowability.

Table 1 Quantified acid sites of the prepared SBA-15-MPSBS

Catylst	TEOS/TESBS(g/g)	pH	Aging temperature (℃)	Aging time (h)	Template (P123, g/100ml)	Acid sites (mmol/g
SBA-15-MPSBS(2)	98/2	<<1	100	48	8	0.53
SBA-15-MPSBS(5)	95/5					0.64
SBA-15-MPSBS(10)	90/10					0.73
SBA-15-MPSBS(20)	80/20					0.97
SBA-15-MPSBS(30)	70/30					1.40
SBA-15-MPSBS(20)	80/20	1				1.01
		2				1.32
		3				1.45
		7				1.11
		<<1	80			0.85
			90			1.00
			110			0.99
			100	24		0.68
				72		0.89
				96		0.95
				48	0.5	0.90
					1	1.01
					10	0.85

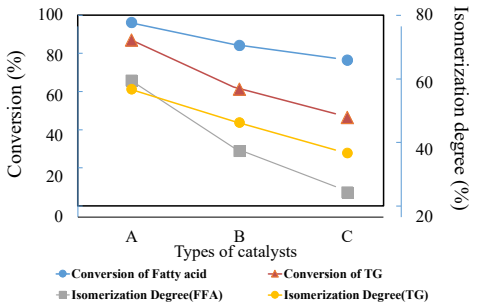


Fig. 1 Results of Conversion of FFA、TG、Selectivity of isomerized Substances and the rate of Isomerization by different temperature. A : SBA-15-MPSBS(10)，B : SBA-15-MPSBS(5)，C : SBA-15-MPSBS(2)

References

[1] Purnanand Vishwanathrao Bhale. Renewable Energy Volume 34, Issue 3, March 2009, Pages 794-800.
[2] Reaume, S.J. and Ellis, N. (2011). J Am Oil Chem Soc, 88: 661-671.
[3] Gerhard Knothe. Fuel，2005，84(9):1059－1065.
[4] Vladimir L. Zholobenko.Advances in Colloid and Interface Science Volume 142, Issues 1–2, 1 October 2008, Pages 67-74.
[5] AOCS Official Method Cc 3-25 .

Designing Holistic Biorefinery Solutions: Process Optimisation and Technoeconomic Viability of Glycerol derived High Energy-Density Fuel Additives

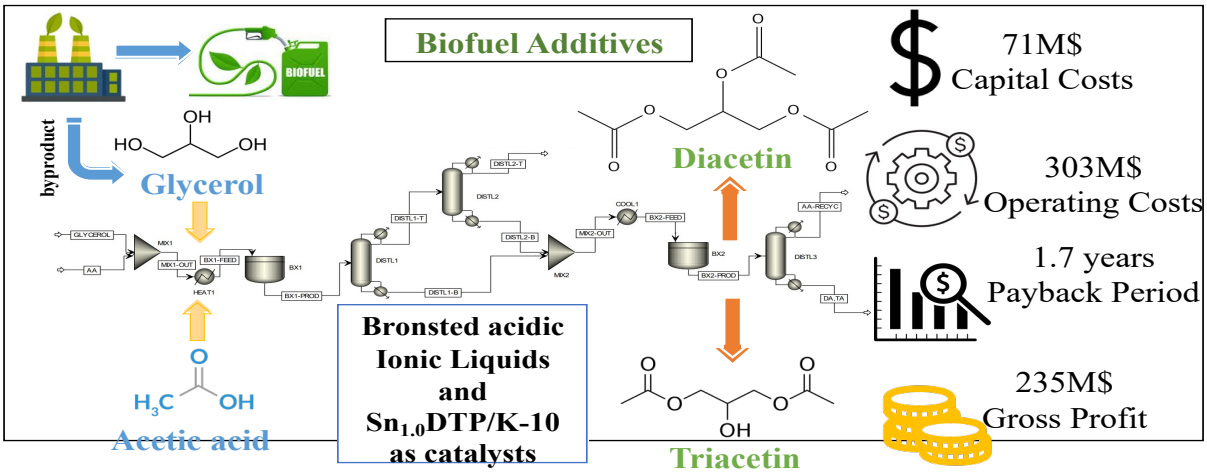
John KEOGH, Manish TIWARI, Callum JEFFREY, Krutarth PANDIT, and Haresh Manyar*
School of Chemistry and Chemical Engineering, Queen's University Belfast, David-Keir Building, Stranmillis Road, Belfast, BT9 5AG, UK.
*Email: h.manyar@qub.ac.uk

Significance and Relevance

This work presents a comprehensive study aimed at designing holistic solutions for the biorefinery industry, with a particular focus on enhancing both the economic viability and environmental sustainability of biodiesel production. The research emphasizes the integration of innovative catalytic technologies and advanced processes for glycerol esterification. Utilizing Design of Experiment (DoE) methodologies, this study delves into multifaceted approaches that optimize critical process parameters. Furthermore, it conducts kinetic studies based on the Langmuir-Hinshelwood (L-H) dual-site model to better understand the reaction mechanisms involved. To facilitate thorough process simulation, Aspen Plus® is employed, providing insights into operational efficiencies and potential bottlenecks. A detailed techno-economic assessment paired with sensitivity analysis has been conducted for a facility designed to produce di- and tri-acetins via a two-stage process, leveraging an annual feedstock of 100,000 tonnes of glycerol. This rigorous exploration underscores the potential for significant advancements in biorefinery operations by optimizing production pathways that not only reduce costs but also minimize environmental impact by truly embracing the concept of circular economy by blending di- and triacetins into the biodiesel pool effectively.

Introduction and Motivations

With increasing energy demand, decreasing fossil fuel reserves, and climate emergency it is imperative to develop renewable biofuels and fuel additives. One of the potential alternatives is the bio-refinery concept, where biodiesel serves as a replacement of fossil fuels. However, bio-diesel production is associated with formation of up to 10wt% of waste glycerol as a liability. To enhance economic viability of biorefineries, it is essential to add value to glycerol, for instance, glycerol esterification using renewable acetic acid. Glycerol esters have a wide range of applications, both di- and tri-acetins are effective as high energy-density fuel additives, improving the combustion and fuel economy of the biodiesel, whilst also decreasing harmful emissions. Glycerol esters can be directly blended into the biodiesel to enhance the carbon atom economy associated with its production, promoting efficient resource utilization, improving process economics as well as the environmental sustainability.



Results and Discussion

Typically, esterification process requires stoichiometric use of mineral acids or $AlCl_3$ as catalyst. With increased importance placed on green chemistry, catalysts need to be safe, non-corrosive and recyclable. In this work, it has been shown that low-cost and commercially available Bronsted acidic ionic liquids are efficient and reusable liquid acid catalysts for esterification. In particular, using [H-NMP][HSO_4] as catalyst, the glycerol esterification was accomplished with 99% conversion of glycerol within 30 minutes, with 97.6% yield of di- and triacetin fuel additives.[1] For optimisation of the glycerol esterification process, the Design of Experiments (DoE) approach was applied, taking into account the variables such as speed of agitation, reaction temperature, glycerol:acetic acid mole ratio and catalyst loading. Herein, we also compared the efficacy of Bronsted acidic ionic liquids as catalysts with solid acid catalyst, such as tin exchanged tungstophosphoric acid (DTP) supported on montmorillonite K-10. Partially, exchanging the H^+ ion of DTP with Sn (x = 1) increased the acidity of the catalyst and showed an increase in the catalytic activity. Different process parameters were optimised, and a suitable kinetic model was fitted. Langmuir-Hinshelwood (L-H) dual-site model was able to describe the experimental data with high agreement between the experimental and calculated results.[2] Furthermore, we have studied the economic feasibility of a facility producing di- and tri-acetins by a two-stage process using 100,000 tonnes of glycerol per year using Aspen Plus®. The analysis indicates that the capital costs are 71 M$ while the operating costs are 303 M$/year. The gross profit is 60.5 M$/year while the NPV of the project is 235 M$ with a payback period of 1.7 years. Sensitivity analysis has indicated that the product price has the most impact on the NPV.[3]

Materials and Methods

The ionic liquids used in this study were prepared and characterized in QUB. For example [H-NMP][HSO_4] was prepared by adding sulfuric acid (9.8 g, 0.1 mol) dropwise slowly to n-methyl-2-pyrrolidone (9.9 g, 0.1 mol) in an ice bath under stirring. Once completed the reaction is carried out for 4 hr at 40°C. The formed ionic liquid was washed with ethyl acetate (3 x 10 mL), and water was removed under reduced pressure. The ionic liquids were characterized using nuclear magnetic resonance (NMR). All synthesized ionic liquids showed high purity. Esterification of glycerol with acetic acid was conducted in a 100 mL two-necked round bottomed flask. In a typical experiment, the reactor was charged with ionic liquid (2 mol %), glycerol (5 g) and acetic acid (19.56 g) and stirred using a magnetic stirrer at 100°C. The reactions were monitored by taking regular samples and analyzed using gas- chromatography (Agilent Technologies 7820A) equipped with FID detector and HP-5 capillary column. The products were identified by GC-MS.

Tin exchanged tungstophosphoric acid supported on K-10 catalysts (20%w/w Sn_1-DTP/K-10) was prepared by sequential incipient wetness technique using Sn(II)Cl_2 and DTP solutions in methanol as precursors. The as prepared materials were dried at 120°C, followed by calcination at 300°C for 3h in tubular furnace under flowing air.

References

1. J. Keogh, M. S. Tiwari, H. Manyar, Ind. Eng. Chem. Res., **2019**, *58* (37), 17235–43.
2. J. Keogh, C. Jeffrey, M. S. Tiwari, H. Manyar, Ind. & Eng. Chem. Res., **2023**, *62*, 45, 19095–19103.
3. K. Pandit, C. Jeffrey, J. Keogh, M. S. Tiwari, N. Artioli, H. Manyar, Ind. Eng. Chem. Res. **2023**, *62*, 23, 9201–9210.

Acknowledgements

The authors gratefully acknowledge the financial support from “The Bryden centre for advanced marine and bio-energy research” funded through the INTERREG VA Programme for PhD studentship to JK. HM thankfully acknowledges the funding and support provided by the UK Catalysis hub via our membership of the UK Catalysis Hub Consortium funded by EPSRC grant: EP/R026645/1, and Queen’s University Belfast for EPSRC QUB Impact Acceleration Award S3189CCE.

Catalyst deactivation in green hydrotreaters: Impact of catalyst composition

Elham Nejadmoghadam*,[1] Olov Öhrman [2], Derek Creaser [1], Louise Olsson[1]
[1] *Chemistry and Chemical Engineering, Chalmers University of Technology, Gothenburg 41296, Sweden.*
[2] *Preem AB, Gothenburg SE-418 23, Sweden.*
* *louise.olsson@chalmers.se*

Significance and Relevance

The findings in this study can be employed to design a guard bed positioned upstream from a catalytic reactor to protect the main catalyst bed from impurities or poisons in the feed stream from bio-origin during hydrotreatment process. Adding metals to guard beds can reduce coking, minimizing pressure drop and surface area loss. This enhancement also improves poison trapping efficiency, extending the main catalyst's lifetime and increasing the removal of inorganic compounds.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion; Circular economy

Preferred presentation: Oral preferred

Introduction and Motivations

Understanding and addressing catalyst deactivation is essential for enhancing the longevity and efficiency of hydrodeoxygenation (HDO) processes in biofuel production from biobased feedstocks. Numerous studies have examined main causes of catalyst deactivation, including coking, metal/sulfur leaching, and sintering [1-4], while studies on poisoning from impurities in bio-oil feedstocks—such as metallic and non-metallic elements acting as catalyst poisons—remain limited. This study aimed to understand the individual contributions of active metals and supports, including $NiMo/Al_2O_3$, $NiMo/SiO_2$-Al_2O_3, and NiW/Al_2O_3, along with bare supports Al_2O_3, SiO_2-Al_2O_3, and zeolite Y (CBV-600), on the deactivation caused by the deposition of poisons after several months of operation in an industrial refinery for renewable biofuel production, as well as to elucidate how poisons affect catalyst properties.

Materials and Methods

Nickel-molybdenum catalysts supported on alumina and silica-alumina ($NiMo/Al_2O_3$ and $NiMo/SiO_2$-Al_2O_3) as well as nickel-tungsten on alumina (NiW/Al_2O_3) were prepared by conventional wetness impregnation. The prepared catalysts along with bare supports including Al_2O_3, SiO_2-Al_2O_3, and zeolite Y (CBV-600) were placed in an industrial refinery unit for renewable biofuel production. After several months of operation, they were extracted from the reactor and sent to our laboratory for analysis of their elemental composition and textural characteristics.

Results and Discussion

The properties of the spent catalysts after being used in the refinery are presented in Figure 1. The key poisons in spent bimetallic catalysts and bare supports were phosphorous (P) and alkali metals (potassium (K) and sodium (Na)). NiW/Al_2O_3 had the highest concentrations of all poisons except K, indicating a greater propensity to absorb poisons. However, bare supports trapped fewer poisons, suggesting active metals attract poisons more than supports alone. Interestingly, bare supports showed higher coking (16-20 wt% vs. 1.1-6.4 wt%), potentially blocking reactants and reducing poison adsorption. Following the refinery run, all bimetallic catalysts lost surface area, with $NiMo/SiO_2$-Al_2O_3 showing the highest loss (18%). Bare supports showed a similar trend but with more severe surface area loss (up to 89%).

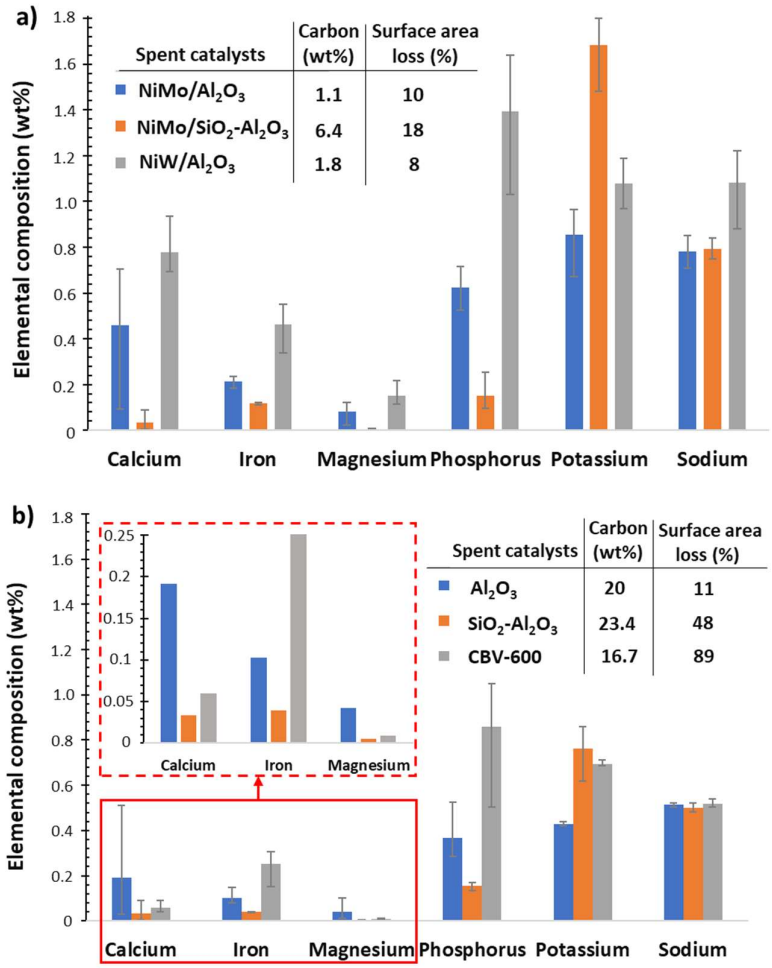


Figure 1 Chemical composition (carbon wt%), the percentage loss of surface area, and concentration of poisons in spent catalyst samples: a) bimetallic catalysts, and b) bare supports.

References

1. Y.W. Cheah, M.A. Salam, J. Sebastian, et al., J. Environ. Chem. Eng. (2023) 109614.
2. Y. Zhou, J. Remon, Z. Jiang, et al., Green Energy & Environment, (2023) 722-743.
3. R. Shomal and Y. Zheng, Nanomaterials, (2023) 13, 2845.
4. T. Cordero-Lanzac, R. Palos, I. Hita, et al., Appl. Catal. B: Environ, (2018) 513-524.

Acknowledgements

This work has been performed at the Competence Centre for Catalysis (KCK) and the Chemical Engineering division at the Chalmers University of Technology in collaboration with Preem. The Competence Centre for Catalysis is hosted by Chalmers University of Technology and financially supported by the Swedish Energy Agency (Project No. 52689-1) and the member companies Johnson Matthey, Perstorp, Powercell, Preem, Scania CV, Umicore, and Volvo Group. We would also like to Acknowledge Formas (FR-2021/0005) for the funding and Swedish Energy Agency (P2023-01506).

Spent Lithium Cobalt Oxide Batteries: Heterogeneous Catalyst for Upcycling Lignocellulosic Biomass

Emilia PAONE*[,1,2], Giulia Maria ITRI[1], Francesco MAURIELLO[1]
[1] *Dipartimento DICEAM, Università degli Studi Mediterranea di Reggio Calabria, IT89123*
* *emilia.paone@unirc.it*

Significance and Relevance

This study adopts a waste-to-resource approach by repurposing spent lithium cobalt oxide ($LiCoO_2$ or LCO) batteries, part of a growing waste stream exceeding millions of units annually, as a heterogeneous catalyst for upcycling lignocellulosic biomass. The cobalt content, a high-value transition metal with remarkable catalytic properties for reductive reactions, is effectively utilized, offering a sustainable alternative to traditional catalysts. The findings highlight a dual benefit: reducing the environmental burden of hazardous battery waste while transforming it into a valuable resource for biomass conversion into high-value chemicals, promoting circular economy principles.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion
Preferred presentation: (Oral only)

Introduction and Motivations

The rapid proliferation of lithium-ion batteries, fueled by their extensive use in electronic devices and electric vehicles, has led to a growing challenge in managing spent lithium cobalt oxide (LCO) batteries.[1] These batteries not only contribute to environmental hazards due to toxic components but also represent a wasted resource, as cobalt is a critical and valuable metal known for its catalytic properties in various chemical processes.[2] Addressing this dual concern, the repurposing of spent batteries into heterogeneous catalysts aligns with sustainable waste management and circular economy principles, enabling both environmental remediation and resource recovery.[3] This innovative approach can unlock new pathways for converting lignocellulosic biomass into value-added products, thereby contributing to renewable energy and material production goals.

Materials and Methods

The cathodic material, also known as “Black Mass” (BM), was obtained through the direct recovery of spent LCO batteries. BM was further processed using a simple mechano-thermal treatment to convert it into an efficient heterogeneous Co-catalyst, which was subsequently fully characterized through XRD, FT-ATR, in-situ DRIFT, XPS, SEM-EDX and TEM analysis.

Reactions were performed in a stainless-steel autoclave reactor (100 mL). In each reaction, 40 mL of a 0.1 M furfural (FUR) solution and 0.25 g of the BM catalyst were loaded into the autoclave, both in the presence and absence of added hydrogen.

Results and Discussion

The performance of spent LCO batteries, as heterogeneous catalysts for the hydrogenation of furfural (FUR) was evaluated under reductive conditions, using 2-propanol as both solvent and hydrogen donor. The study revealed promising catalytic activity, with significant conversion of furfural to furfuryl alcohol (FAL).

In fact, under optimized conditions (2-propanol, H_2 pressure of 10 bar, 210 °C, and 180 minutes of reaction), a conversion of 65% to FAL was achieved. Extending the reaction time further improved FUR conversion to 90%, although a decline in catalyst stability was observed due to cobalt leaching (Figure 1).

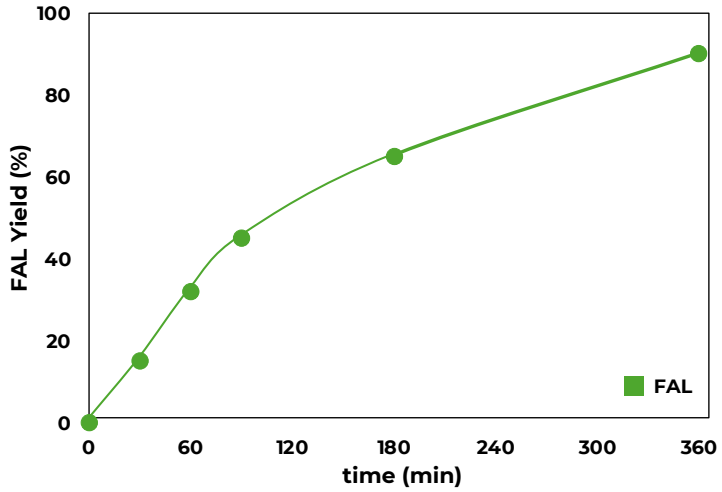


Figure 1. Reaction time effect on furfural hydrogenation [reaction conditions: FUR 0.1 M; 2-PrOH, H_2 10 bar; 210 °C]

Higher reaction temperatures, up to 240 °C, enhanced conversion rates and selectivity, but also exacerbated catalyst degradation, as indicated by increased cobalt leaching (Figure 2).

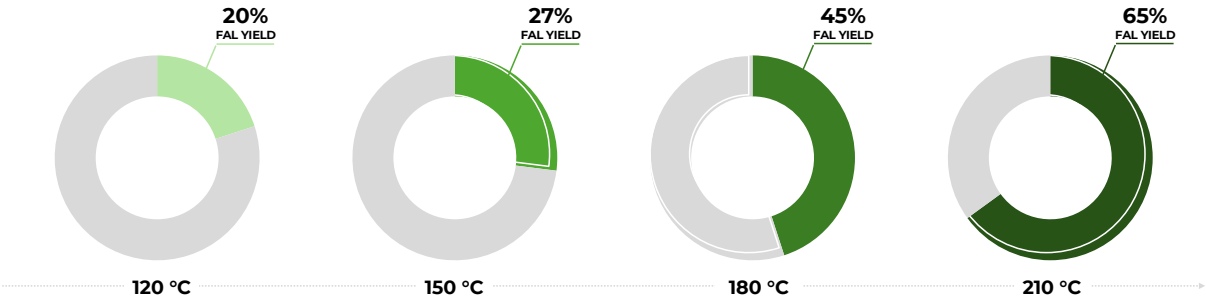


Figure 2. Reaction Temperature effect on furfural hydrogenation [reaction conditions: FUR 0.1 M; 2-PrOH, H2 10 bar; 180 min]

Importantly, no by-products were detected under any of the tested conditions, demonstrating the catalyst's high selectivity. These findings highlight the effectiveness of BM-derived catalysts in biomass upcycling while emphasizing the need for strategies to mitigate catalyst degradation during prolonged and high-temperature reactions.

High furfural conversion can also be obtained under transfer hydrogenation conditions by using 2-propanol as solvent/H-donor. Finally, in order to extend the substrate scope, hydrogenations of other lignocellulosic derived molecules were also tested, clearly show that spent LOC can be efficiently used as a heterogeneous catalyst for their reductive upgrading. In this contribution, we present a novel approach to re-use spent LCO as a stable and efficient Co-based heterogeneous catalyst, demonstrating its high activity for the selective reductive upgrading of biomass-derived molecules.

References

1. B.K. Biswal, B. Zhang, P.T.M. Tran, J. Zhang, R. Balasubramanian, *Chem. Soc. Rev.* **2024**, *53*, 5552-5592.
2. C. Xu, E. Paone, D. Rodríguez-Padrón, R. Luque, F. Mauriello, *Chem. Soc. Rev.* **2020**, *49 (13)*, 4273-4306.
3. E. Paone, M. Miceli, A. Malara, G. Ye, E. Mousa, E. Bontempi, P. Frontera, F. Mauriello, *ACS Sustainable Chem. Eng.* **2022**, *10*, 2275−2281.

Conversion of glucaric acid to adipic acid by Pd−ReO_x catalyst supported on carbon-based materials

Rosalba PASSALACQUA*[1], Salvatore ABATE[1], Siglinda PERATHONER[1], Gabriele CENTI[1], Alfredo ALOISE[2], Cristiano MAESANIi[3], Claudia CASTELLI[3], Stefano ALINI[3]

[1] *University of Messina, Department of Chemical, Biological, Pharmaceutical and Environmental Sciences (ChiBioFarAm) & INSTM CASPE (Lab. of Catalysis for Sustainable Production & Energy, Viale F. Stagno d'Alcontres 31, 98166 Messina, Italy*
[2] *Department of Physical and Chemical Sciences, University of L'Aquila, via Vetoio, Coppito 2 67100 L'Aquila, Italy*
[3] *Radici Group, Via G. Fauser, 50, Novara 28100 - Italy*

** rpassalacqua@unime.it*

Significance and Relevance

Green Synthesis of adipic acid from renewable biomass is a topic of industrial interest and a very challenging goal of sustainable chemistry, therefore the development of highly efficient catalysts able to catalyze the reaction are highly desired. In fact, adipic acid represents a key monomer for the synthesis of one of the most important polymers intermediates in the chemical industry, nylon-66.

- *Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion /*

Preferred presentation: Short Oral

Introduction and Motivations

Adipic acid production from renewable biomass is a very challenging goal of green chemistry. Here we report on the performance of a bifunctional Pd−ReO_x catalyst used for the sustainable synthesis of adipic acid via glucaric acid. Glucaric acid represents the oxidation product in the transformation of cellulose-derived glucose and, at the same time, the reagent of a second challenging step-reaction of deoxydehydration (DODH) for obtaining adipic acid. An activated carbon-supported bifunctional catalyst composed of palladium and rhenium oxide is reported to be powerful for the removal of four hydroxyl groups in glucaric acid, affording adipic acid with high yield.[1] This work presents the performance of the Pd−ReO_x bifunctional-catalyst supported on different carbonaceous materials highlighting the role of the support for an efficient deoxygenation in the adipic acid synthesis.

Materials and Methods

The bifunctional catalyst composed of Pd metal and rhenium oxide, co-loaded on activated carbon (0.5% Pd−10% ReO_x/AC) was prepared by a co-impregnation method. Four different commercially available activated carbons (AC) were tested as support: XC-72, Charcoal activated (Supelco), Chemviron F300, Norit-Hydro Darco GCW granular carbons crushed and reduced to powder.

AC (1.0 g) was first mixed with an aqueous solution of NH_4ReO_4 and $Pd(NO_3)_2$ at room temperature under continuous stirring. After stirring for 12 h, the solvent was evaporated at 353 K to get a solid product. The solid product was subsequently dried at 383 K for 12 h. Then, the Pd−ReO_x/AC catalyst was obtained by heating the solid product at a rate of 2 K min^{-1} to 673 K and keeping at 673 K for 3 h under N_2 flow (40 mL min^{-1}). The loading amount of metal oxides ReO_x, and Pd nanoparticles were fixed at 10.0 wt% and 0.5 wt%, respectively for the best case, but also other loads were investigated.

The glucaric acid conversion has been carried out in a 300mL autoclave using the following experimental setup: 700 mg of catalyst, 875 mg of D-glucaric acid potassium salt, 1400 mg of Amberlyst-15, and 175 mL of methanol were first added into the reactor. After purging with H_2 five times, the reactor was charged with 2 MPa of H_2 at room temperature. Then, the reaction started by heating the reactor to 383 K in an oil bath. After 24 h, the reaction was stopped by cooling the reactor to room temperature in cold water. The liquid products were analyzed with a GC (GC-7890B, Agilent)

by using dimethyl succinate as an internal standard, the yields were reported as percentage of dimethyl adipate (% DMA).

Results and Discussion

The prepared catalysts have been characterized by XRD, SEM, XPS, and physisorption measurements.

In the mixed Pd−ReO_x catalysts, the deoxygenation operated by the rhenium oxide functions was synergically facilitated by the copresence of Pd which catalyzes the hydrogenation of the olefin intermediates and promotes the removal of four hydroxyl group (deoxygenation).

In the carbon-based samples investigated, micro and mesopores have been observed. A linear correlation was observed between the mesoporous volume (V_{meso}) typical of the catalysts shown in **Table 1** and the yield of dimethyl adipate (%) obtained from the catalytic conversion of potassium glucarate.

Table 1. *Physisorption characteristics of the investigated catalysts and conversion yields to DMA.*

SAMPLE	Composition	BET [m^2/g]	V_{micro}	V_{tot} [cm^3/g]	V_{meso}	DMA yield (%)
Cat-2	Pd−ReO_x_AC_Charcoal	643	0.18566	0.39998	0.21432	41.3
Cat-3	Pd−ReO_x_AC_Hydro_Darco	909	0.29069	0.44870	0.15801	31.8
Cat-4	Pd−ReO_x_AC_VironF300	710	0.22968	0.31873	0.08905	24.1

The sample with the highest mesoporosity (Cat-2) is also the one with the highest DMA yield. In fact, from the comparison with the yield of Cat-3, which has a greater surface area, and a greater volume of micropores, compared to that of mesopores, it is evident that the best performances correlate with the presence of higher volumes of mesopores.

References

1. W. Deng, L. Yan, B. Wang, Q. Zhang, H. Song, S. Wang, Q. Zhang, Y. Wang. *Angew. Chem. Int. Ed.,* **2021**, 4712-4719.

Acknowledgements

This work has been supported by the European Union's Horizon 2020 research and innovation programme under grant agreement No. 820723 (PERFORM Project).

Sulfonated metal oxide catalysts for the cascade conversion of levulinic acid to isopropyl levulinate and γ-valerolactone

Marco RUSSO*, Chiara ALIOTTA, Valeria LA PAROLA, Giuseppe PANTALEO, Maria Luisa TESTA
Institute of Nanostructured Materials, ISMN-CNR, Via Ugo La Malfa 153, 90146 Palermo, Italy.
* marco.russo@cnr.it

Significance and Relevance

In the present work, the acid-catalyzed conversion of levulinic acid to isopropyl levulinate and γ-valerolactone, using isopropanol as hydrogen donor, was investigated. The activity of several sulfonated catalysts supported on metal oxides (SiO_2, Al_2O_3, TiO_2, ZrO_2) was evaluated. The preliminary results obtained showed that the different amount of acid sites on the catalyst and their Bronsted-Lewis features were discriminating to catalyze the synthesis of isopropyl levulinate and γ-valerolactone by a cascade conversion of levulinic acid. These types of catalysts have the advantage of not having a reduced metal phase and thus not requiring controlled atmosphere conditions.

Preferred topic: Green chemistry and biomass transformation, renewable resources conversion
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Today, it is sometimes thought that to address the problems of the energy scenario (demand, sustainability, and feasibility), find a single energy solution or approach is mandatory and as consequence, we often hear about "electrification" or "hydrogen economy." Rather, the solution to deal with this context is to take advantage of different approaches. A clear example is the transportation sector, where electrification cannot cover all energy density requirements for different vehicles and hydrogen cannot be easily introduced into the current distribution and supply network. For these reasons, e-fuels and newly developed biofuels can play a key role. In the case of biomass-derived fuels, the first challenge is to reduce the oxygen-to-carbon ratio of platform molecules (fructose, glucose, HMF, levulinic acid) using an efficient and selective catalytic process that requires as little hydrogen as possible.

In this context the conversion of levulinic acid to γ-valerolactone (GVL) is a process of interest due to the potential application of GVL spanning from green solvent, intermediate for polymers production, fuels additives and precursors for liquid biofuels.

GVL is usually obtained by metal catalysed reduction of levulinic acid using molecular H_2. This approach takes advantage of the use of heterogeneous nobel metal catalysts such as Pd, Pt [1], PdAu [2,3], Ru [4]. The use of nobel metals allows to achieve high yield of GVL, but they suffer of deactivation as well as to be expensive. For these reasons many efforts have been done to use non-nobel metals (Ni, Cu, Zr, Al etc., [5]) as reduction catalysts. Non-nobel metal catalysts were also extensively studied to catalyze the reduction of levulinic acid by catalytic transfer hydrogenation (CTH) which use hydrogen donor molecules, usually secondary alcohols circumventing in such a way the issues (high temperature and pressure) related to the use of gaseous hydrogen. For the CHT process several non-nobel metallic phase supported on metal oxide were studied to find the better compromise between Lewis and Bronsted acid sites necessary to catalyze the hydrogen transfer, between donor alcohol and levulinic acid, and the intramolecular cyclization to GVL. The problem with this type of catalyst is that the presence of the metal phase requires working in a controlled atmosphere. In literature are reported only few examples of catalysts without the presence of metallic phase.[6,7]

Materials and Methods

Metal oxide supports were synthesized by templated sol-gel synthesis as reported in previous works.[8] Support-SO3H catalysts were synthesized by grafting procedure. In a typical synthetic procedure, chlorosulfonic acid (0.25 mL, 3.6 mmol) was added dropwise to a suspension of desired dried support (1.0 g, 1.2 mmol) in dry dichloromethane (10 mL) at 0 °C stirring for 2 h until the HCl gas evolution

stopped. Then, the mixture was filtered and washed with ethanol and dried at room temperature to obtain support–SO3H materials.

In a typical catalytic test, the reaction mixture composition was 3.8 mL of isopropanol (2.98 g, 49.7 mmol), 50 µL of levulinic acid (LA, 56.7 mg, 0.49 mmol, molar ratio isopropanol:LA = 100), a catalyst amount between 10 - 20 wt% with respect to starting levulinic acid weight. The tests were performed in screw cup glass vials at different temperature and time under stirring.

The reaction mixture was analysed by GC-FID to assess LA conversion as well as yield and selectivity to isopropyl levulinate and γ-valerolactone.

Results and Discussion

From preliminary catalytic tests, carried out at 120, 150 and 160 °C for 3h using 10wt% of catalyst, an increase of conversion of LA and the yield of IsoPrLev with the reaction temperature was observed. The yield of IsoPrLev follows the profile of acidity of the catalysts, whereas it is worth noting that only with ZrO_2 based catalysts, GVL product was observed.

This finding highlights the importance of the need of Bronsted and Lewis acid sites to carry out the conversion of levulinic acid to γ-valerolactone. The Zr lewis acid sites can coordinating the oxygen atoms of isopropanol and ketonic oxygen of Levulic acid favouring the hydrogen transfer and $-SO_3H$ Bronsted acid site can promote the intramolecular cyclization of 4-hydroxypentanoic acid (or 4-hydroxypentanoic acid isopropyl ester) to give γ-valerolactone. Although the low yield of γ-valerolactone obtained this result is promising due to the low amount of catalyst used with respect to comparable catalyst reported in literature.[6,7]

The preliminary results highlight that heterogeneous acid catalysts, without metallic active site, can promote the cascade conversion of levulinic acid to γ-valerolactone. The selectivity of the latter can be improved by modulating the Bronsted and Lewis acidity of the catalyst.

References

1 P. P. Upare, J. M. Lee, D. W. Hwang, S. B. Halligudi, Y. K. Hwang, J. S. Chang, *Journal of Industrial and Engineering Chemistry* **2011**, *17*, 287.

2 M. L. Testa, L. Corbel-Demailly, V. La Parola, A. M. Venezia, C. Pinel, *Catal Today* **2015**, *257*, 291.

3 N. S. Date, V. La Parola, C. V. Rode, M. L. Testa, *Catalysts* **2018**, *8*.

4 A. M. R. Galletti, C. Antonetti, V. De Luise, M. Martinelli, *Green Chemistry* **2012**, *14*, 688.

5 S. Dutta, I. K. M. Yu, D. C. W. Tsang, Y. H. Ng, Y. S. Ok, J. Sherwood, J. H. Clark, *Chemical Engineering Journal* **2019**, *372*, 992.

6 Y. Kuwahara, W. Kaburagi, Y. Osada, T. Fujitani, H. Yamashita, *Catal Today* **2017**, *281*, 418.

7 J. Song, B. Zhou, H. Zhou, L. Wu, Q. Meng, Z. Liu, B. Han, *Angewandte Chemie* **2015**, *127*, 9531.

8 M. L. Testa, M. L. Tummino, A. M. Venezia, M. Russo, *Materials* **2023**, *16*.

Model molecule investigation for the reductive catalytic fractionation of lignin using innovative magnetic catalysts

Federico BUGLI[1], Giuseppe SALIERNO[1,2], Fabrizio CAVANI[1,3], Tommaso TABANELLI[*,1,3]
[1] *University of Bologna, "Toso Montanari" Department of Industrial Chemistry, Via Piero Gobetti 85, 40129, Bologna, Italy.*
[2] *University of Perugia, Department of Chemistry, Biology and Biotechnology, Via Elce di Sotto 8, 06132, Perugia, Italy. PERUGIA*
[3] *University of Bologna, Center for Chemical Catalysis - C[3], Via Piero Gobetti 85, 40129, Bologna, Italy.*
** tommaso.tabanelli@unibo.it*

Significance and Relevance

Herein, we investigated the use of model molecules to provide fundamental insights into the catalytic behavior of a RuOx/γ-Fe_2O_3, recently published by our group as suitable catalyst in the reductive catalytic fractionation (RCF) of poplar sawdust[1], highlighting the critical influence of catalyst support on the products distribution achievable. In the catalytic hydrogenation of these compounds, the reaction mechanism is typically governed by the adsorption geometry of the molecule, traditionally linked to metal nanoparticles (NPs) size[2]. However, our findings suggest that it is the type of support that shapes the adsorption behavior and directs the reaction pathways.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion; Circular economy.

Preferred presentation: Oral preferred

Introduction and Motivations

The sustainable valorization of lignocellulosic biomass (LCB) is still a challenge for the chemical industry. In this context, lignin first biorefineries is a suitable approach in order to valorize all the structural components of LCB, including lignin[3]. Efficient lignin depolymerization and stabilization (i.e. in reducing environments) targets β-O-4 ether linkages to produce bio-based, aromatic monomers while minimizing recondensation[4]. Model molecules simplify the reaction environment, replicating lignin's key features, enabling controlled studies of reaction mechanisms, catalyst efficiency, and conditions optimization.

Materials and Methods

Model molecules were selected to evaluate the Reductive Catalytic Fractionation (RCF) process, focusing on catalytic performance in suppressing recondensation and promoting bond cleavage. Eugenol and vanillin were used to study recondensation suppression, while a dimer with a β-O-4 bond (2-phenoxy-1-phenylethanol, 2P1P) was employed to investigate the ether bond cleavage. An innovative RuOx/γ-Fe_2O_3 was synthesized via Incipient Wetness Impregnation of a commercial magnetite and calcinated at 400°C, along with other noble metals to assess their effect. Under the reducing reaction environment, the former RuOx/γ-Fe_2O_3 is reduced in-situ, forming the active Ru/Fe_3O_4 which allows for magnetic separation during downstream processes. Commercial Ru/C served as a benchmark for comparison. The catalytic tests were performed in a batch reactor (autoclave) using operational parameters to best represent the reaction conditions recently reported on real biomass (solvents, catalyst/substrate ratio etc.)[1].

Results and Discussion

The catalytic performance of RuOx/γ-Fe_2O_3 and Ru/C was evaluated using 2-phenoxy-1-phenylethanol (2P1P) as a model molecule to study β-O-4 bond cleavage. Without a catalyst, no significant reaction occurred, highlighting the β-O-4 bond's stability. Both catalysts showed substrate conversion, with Ru/C leading to aromatic ring hydrogenation generating saturated dimers, which hinder further cleavage. In contrast, Ru/Fe_3O_4 facilitates the selective β-O-4 bond cleavage and preserves aromaticity. In this study, the analysis of the catalysts showed that

RuOx/γ-Fe_2O_3 has larger metal NPs compared to Ru/C, which has better dispersion. Interestingly, the activity for β-O-4 bond cleavage contradicts the trends reported in the literature, where better dispersion and smaller NPs sizes are typically associated with orthogonal adsorption. We propose that the oxophilic nature of Ru/Fe_3O_4 might promote orthogonal adsorption via the hydroxyl group, possibly generating and unstable carbocation that foster consecutive ether bond cleavage. On the other hand, Ru/C may favor planar adsorption through the interaction with the π-electrons of the aromatic rings, favoring over-hydrogenation also thanks to the smaller Ru NPs.

Complementary studies with eugenol and vanillin confirmed that both catalysts stabilize reactive groups (alkyl double bond and aldehyde), but with different selectivity. Ru/γ-Fe_2O_3 achieved high yields of stabilized products like 4-propyl guaiacol and 2-methoxy-4-methylphenol respectively, while suppressing undesired aromatic ring saturation. Ru/C displayed broader reactivity, forming a variety of over-reduced products including saturated rings moieties, supporting our previous hypothesis.

By supporting alternative active phases on γ-Fe_2O_3, we found that Pd, like Ru, is effective for β-O-4 cleavage, a behavior already recognized in the context of RCF.

This study highlights the fundamental role of catalyst support in reaction pathways and underscores Pd and Ru supported on γ-Fe_2O_3 as a promising candidate for selective lignin valorization. Further exploration of reaction conditions and catalysts properties could enhance efficiency in real biomass applications.

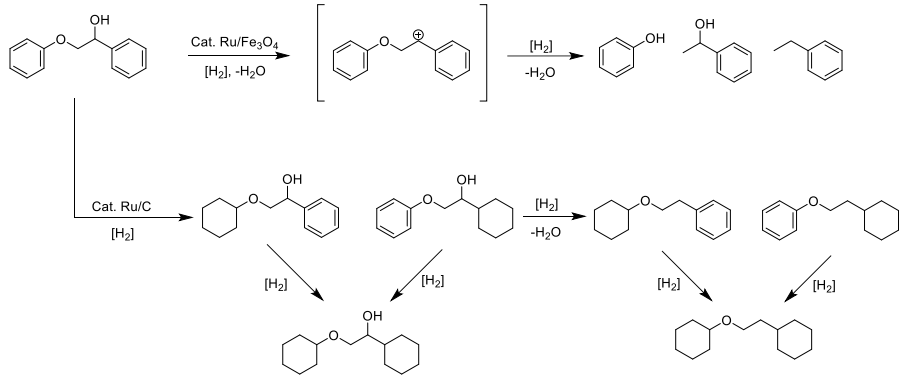


Figure 1 2P1P hydrogenation/hydrodeoxygenation pathway over either RuOx/γ-Fe_2O_3 (active specie Ru/Fe3O4) or Ru/C.

References

1. F. Bugli, A. Baldelli, S. Thomas, M. Sgarzi, M. Gigli, C. Crestini, F. Cavani, T. Tabanelli, ACS Sustainable Chem. Eng. **2024**, 12, 45, 16638–16651.
2. J. Marlowe, P. C. Ford, M. M. Abu-Omar, P. Christopher, Catal. Sci. Technol. **2023**, 13, 5662
3. E. Paone, T. Tabanelli, F. Mauriello. Current Opinion in Green and Sustainable Chemistry, **2020**, 24, 1-6
4. V. K. Garlapati, A. K. Chandel, S. P. J. Kumar, S. Sharma, S. Sevda, A. P. Ingle, D. Pant, Renewable and Sustainable Energy Reviews **2020**, 130, 109977

Acknowledgements

Financed by the European Union - NextGenerationEU through the Italian Ministry of University and Research under PNRR “Piano Nazionale di Ripresa e Resilienza” - Mission 4 “Istruzione e Ricerca” Component 2 “Dalla ricerca all’impresa”, Investment 1.1, “Fondo per il Programma Nazionale di Ricerca e Progetti di Rilevante Interesse Nazionale (PRIN) – Piano Nazionale di Ripresa e Resilienza, addressed to Progetti di Ricerca di Rilevante Interesse Nazionale”. D.D. n. 104 del 2/2/2022, Project title: ENhanced CAtalytic fractionation and depolymerization Processes for a Straightforward valorization of lignocellULosic biomass to chemicals and mATErials (ENCAPSULATE) codice2022KTAH2L - CUP: J53D23007620006.

Exploring $BaTiO_3$-Derived Materials for Advancing SOFC Electrode Performance

Valerie THEUNS*[1], Donovan LEDRU[2], Marie-Hélène CHAMBRIER[2], Aurélie ROLLE[1], Anne-Sophie MAMEDE[1], Héloïse TISSOT[1], Elise BERRIER[1]

[1] *Univ. Lille, CNRS, UCCS – Unité de Catalyse et Chimie du Solide, F-59000 Lille, France.*

[2] *Univ. Artois, CNRS, Centrale Lille, Univ. Lille, UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, F-62300 Lens, France*

** valerie.theuns@univ-lille.fr*

Significance and Relevance

The present work has significance in addressing one of the key challenges in new air-electrode materials for solid oxide fuel cells (SOFCs), the reduction of critical raw materials (CRMs) such as cobalt (Co) and lanthanum (La). By focusing on $BaTiO_3$-derived perovskites, this study contributes to the development of alternative materials with both environmental and economic advantages, focusing on a more sustainable approach to energy conversion technologies. Additionally, this research establishes a methodology of characterization for future novel materials.

Preferred and 2nd choice for the topic: Sustainable and clean energy production and transport. *Second choice:* green chemistry and biomass transformation, renewable resources conversion
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

One of the current challenges in solid oxide fuel cell (SOFC) development is the removal or reduction of critical raw materials (CRMs), like Co, La and Sr[1], in electrode materials while maintaining adequate electrochemical activity and ionic conduction. On the other hand, non-critical alternatives such as barium titanate $BaTiO_3$ (BTO) show significantly lower activity. The objective of the present work is to take advantage of the capability of ABO_3 perovskite oxides to accommodate various cation substitutions at A- and/or B-site to embed the needed functions. In practice, we target the design of BTO-derived perovskites with increased redox activity and improved ionic conductivity, which is a promising starting point for low-CRM materials.

For example, substituting Ti^{4+} by Fe^{3+} at B-site of $BaTiO_3$ is expected to bring additional redox functions, while modifying the total cationic charge leads to structural rearrangements to maintain neutrality. In general, varying the ionic radii, the formal charge of the cations or the A/B ratio is expected to cause structural disorders which can sustain ionic conductivity or favor the ex-solvation of an additional crystal phase.[2] Moreover, A-site deficient perovskite materials have demonstrated improved redox activity over the stoichiometric counterparts.[3]

In this work, we target the selection of BTO-based oxides modified by the substitution of A-site cations (Ba^{2+}) and/or B-site cations (Ti^{4+}). To this end, the following dopants were chosen to substitute the A- and B-sites of BTO, to form a series of BTO-derived samples: Ca^{2+} and La^{3+} ions for the A-site, and Pr^{3+}, Ni^{2+}, Fe^{3+} and Cu^{2+} ions for the B-site.

Our research focuses on a comprehensive investigation of BTO-derived perovskites, examining their structure, including minority phases, redox properties, surface composition and ionic conductivity.

Materials and Methods

The BaTiO3-derived samples were prepared using the citrate complexation method, accompanied by some samples synthesized with the conventional ceramic (solid-state) method and samples made with an autocombustion synthesis.

Several characterization techniques (SSA, TGA-DSC, TPR-TPO, XRD, and XPS) were used. Moreover, operando Raman spectroscopy was run by means of a dedicated environmental cell (Harrick Scientific) and a HR800 Horiba spectrometer equipped with several lasers allowing excitation wavelengths of 633, 532 or 457nm. XPS has been performed by means of a Kratos Analytical Axis UltraDLD spectrometer. Quasi in-situ measurements were made using the catalytic cell, where the

samples were thermally pretreated under gaseous reactant flow at atmospheric pressure and transferred to the analysis chamber under UHV.

Results and Discussion

XRD, Raman, and XPS analyses revealed ex-solved crystalline phases in some of the samples. Preliminary results of a $Ba_{0.85}Ca_{0.15}Ti_{0.80}Fe_{0.20}O_3$ sample show some reducibility by TPR, making it suitable for H2 reduction. Fig. 1 shows in-situ Raman spectra collected during H_2/O_2 cycling. H_2-TPR induced clear spectral modifications beyond thermal effects, notably a shift to lower frequencies, decreased intensity at 505 cm^{-1}, and increased intensity at 730 cm^{-1}. O_2-TPO restored the initial Raman spectrum, indicating sample regeneration upon redox cycling.

The sample's reducibility correlates with its iron content, as evidenced by the quasi in-situ XPS spectra in Fig. 1. Metallic iron is formed after reduction at 800°C and disappears upon reoxidation, suggesting that the observed reduction is linked to Fe cations. Further analysis using complementary techniques will provide a detailed discussion of this phenomenon

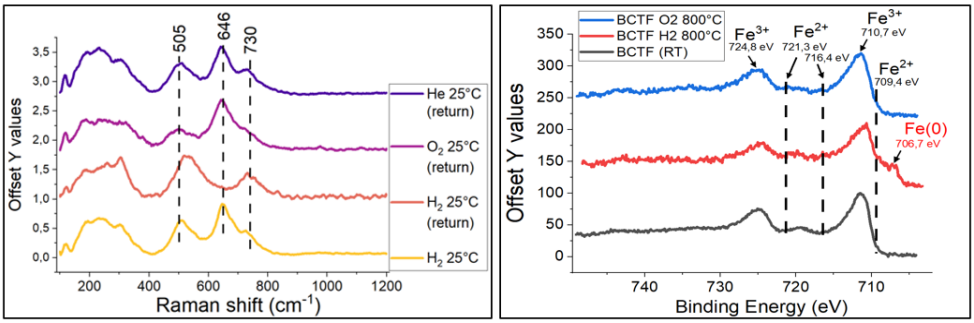


Figure 1. *Left: evolution of the Raman spectra at λ = 633 nm of $Ba_{0.85}Ca_{0.15}Ti_{0.80}Fe_{0.20}O_3$ during in-situ measurements. Right: quasi in-situ XPS spectra of $Ba_{0.85}Ca_{0.15}Ti_{0.80}Fe_{0.20}O_3$ showing the Fe 2p orbitals after H_2 reduction at 800°C and O_2 oxidation at 800°C.*

In conclusion, combining in-situ Raman experiments, XPS measurements, and the other characterization techniques, it becomes possible to estimate the performance of a possible SOFC electrode material. Additionally, the activity of the perovskite materials is influenced by their synthesis method.

References

1. European Commission, (…), Veeh, C., Publications Office of the European Union, **2023**
2. Zakeri, F., (…), Khataee, A., Al-Ce co-doped BaTiO3 nanofibers as a high-performance bifunctional electrochemical supercapacitor and water-splitting electrocatalyst. *Scientific Reports*, **2024**, 14(1), 9833.
3. Sun, Y., (…), Luo, J., A-site deficient perovskite: the parent for in situ exsolution of highly active, regenerable nano-particles as SOFC anodes, *Journal of Materials Chemistry A*, **2015**, 3(20), 11048-11056.

Acknowledgements

This work has been conducted within the framework of the KNOWSKITE-X project; a collaborative research initiative aimed at boosting the development of materials for energy applications. I would like to express my sincere gratitude to the European Union for their financial support, which has made this PhD research possible. I deeply appreciate the opportunities provided by this project to explore and contribute to cutting-edge research.

Magnetic ferrite-based materials for hydrogen generation via water photo-electrolysis

Daniele VALENZISI[1], Falak SHAFIQ[1], Luana DE PASQUALE[*,2], Tatiana RODRIGUEZ-FLORES[1], Roberto NISTICO'[1], Matteo CANTONI[3], Marco MONTALBANO[4], Maria Vittoria DOZZI[4], Mery MALANDRINO[5], Maria Cristina PAGANINI[5], Chiara GENOVESE[2]

[1]*University of Milano-Bicocca, Dept. of Materials Science, Via R. Cozzi 55, Milano, Italy.*

[2]*University of Messina, Dept. of Chemical, Biological, Pharmaceutical and Environmental Sciences, Viale F.S. D'Alcontres 31, Messina, Italy.*

[3]*Politecnico di Milano, Dept. of Physics, Via G. Colombo 81, Milano, Italy.*

[4]*University of Milano, Dept. of Chemistry, Via C. Golgi 19, Milano, Italy.*

[5]*University of Torino, Dept. of Chemistry and NIS Centre, Via P. Giuria 7, Torino, Italy.*

**luana.depasquale@unime.it*

Significance and Relevance

In the present study, magnetic Cu, Co, Ni, and Zn ferrites were synthesized following a co-precipitation approach carried out at mild conditions (*i.e.*, 90 °C, 2 hours), followed by a thermal treatment (*i.e.*, 700 °C, 5 hours). Subsequently, after performing morphological (SEM), structural (XRD), physicochemical (ICP-OES, FTIR spectroscopy), and magnetic (VSM) characterizations, the most promising materials were tested in the photo-induced hydrogen evolution reaction (*photo*-HER) at neutral pH, showing a significant increase in terms of current density under irradiation, and a consequent increase in H_2 productivity. These results, although preliminary, highlight how these systems can be promising photocatalysts for promoting photo-induced HER processes.

Preferred and 2nd choice for the topic:

- Photocatalysis and photoelectrocatalytic approaches, solar energy utilization.
- H_2 storage and transportation, green H_2 production, hydrogen vectors.

Preferred presentation: Poster

Introduction and Motivations

The consumption of fossil fuels represents the current energetic model for the energy production. However, the growing attention toward the challenges related to the energy green transition and the reduction of CO_2 emissions has made the search for alternative technological solutions for the clean energy production an essential current task. In this context, the exploitation of H_2 (better if obtained through green processes, and from renewable sources) is one of the most promising strategies, given its ability to act as a clean energy carrier.[1] Unfortunately, the possibility of exploiting catalytic routes to produce fuels at large scale is still strongly affected by the selection of the best catalyst (hopefully avoiding the use of platinum group metals).[2] In this regard, magnetic spinel ferrite nanomaterials represent a class of magnetic compounds promising for the energy field, due to their high catalytic activity, presence of active surfaces, selectivity toward the hydrogen evolution reaction (HER), and chemical versatility.[3]

Materials and Methods

Magnetic ferrites were synthesized applying a co-precipitation route,[4] by introducing into an aqueous solution containing the desired metallic cations (*i.e.*, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, and Fe^{3+}, fixing the M^{2+}:Fe^{3+} molar ratio equal to 1:2) an alkaline 5 M NaOH solution (precipitating agent). The synthesis took place at constant temperature (90 °C), and time (2 hours). Once purified by performing several centrifugations, and washing runs, solid particles were dried, manually ground, and calcined in a muffle oven at 700 °C for 5 hours.[5] The as-prepared samples, fully characterized, were loaded on a ITO support by drop-casting and tested in photo-electrocatalytic (PEC) HER using a three-electrode compact cell, consisting of two compartments (anodic and cathodic) separated by a Nafion membrane and equipped with a quartz window for irradiation of the catalyst. The produced H_2 was analyzed by gas chromatography (GC) equipped with a TCD.

Results and Discussion

In all cases, XRD analyses confirmed the crystal structure of ferrites. Morphological analysis performed by SEM revealed distinct morphologies for the different samples of ferrites (Figure 1). In detail, bare Cu ferrite ($CuFe_2O_4$) showed the presence of rounded particles (40-600 nm) together with larger anisotropic structures (*ca*. 500 nm), attributable to a secondary phase of CuO (corroborated by XRD and FTIR analyses). Bare Co ferrite ($CoFe_2O_4$) showed the presence of micrometric aggregates with rounded edges and the co-presence of considerably small particles (few tens of nm). Both bare Ni ($NiFe_2O_4$) and Zn ($ZnFe_2O_4$) ferrites, instead, showed needle-like structures, with average diameters of *ca*. 450 nm, and *ca*. 100-500 nm, respectively. Magnetic characterization highlighted an overall superparamagnetic behavior for all bare ferrites, with a hint of hysteresis in the case of Co ferrite, and a weak magnetic response in the case of Zn ferrite. Magnetic saturation values follow the order $CoFe_2O_4$ (55.7 emu g^{-1}) > $CuFe_2O_4$ (31.3 emu g^{-1}) > $NiFe_2O_4$ (18.7 emu g^{-1}) > $ZnFe_2O_4$ (6.4 emu g^{-1}).

A comparative study was carried out over different spinel ferrites to thoroughly investigate the effect of M = Cu, Co, Ni, and Zn on water photo-electrolysis at neutral pH. Among all the catalysts tested, Cu and Zn ferrites demonstrated the most impressive performances. Specifically, $CuFe_2O_4$ exhibited the highest Faradaic Efficiency (FE of 87%) over three hours of photo-electrocatalytic testing (with a correspondence hydrogen evolution rate of 75 mmol h^{-1} g^{-1}). This interesting performance can be attributed to the superior photocurrent response of $CuFe_2O_4$ compared to the other ferrite-based materials. Under light irradiation, there was a significant increase in current density (more than 15% compared to the dark) which is crucial for enhancing the overall efficiency of the photo-electrolysis process.

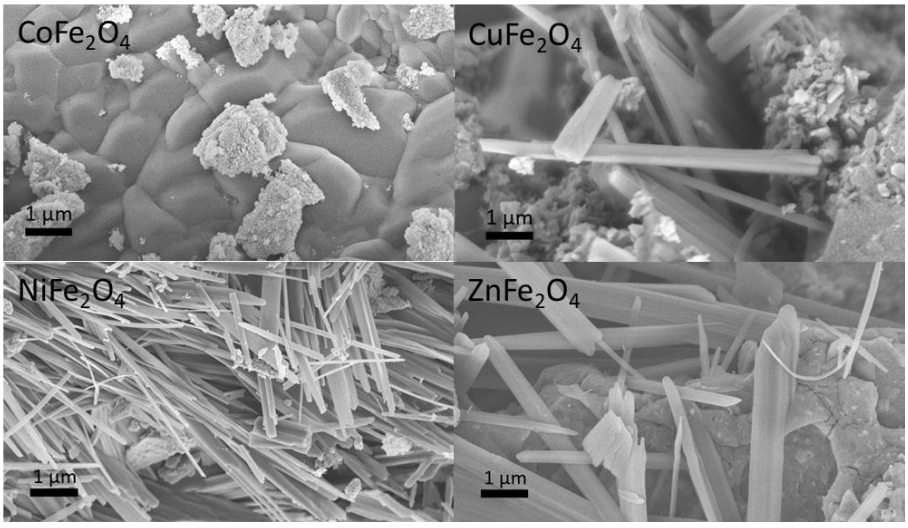


Figure 1 SEM micrographs of magnetic ferrites.

References

1. G. Centi, S. Perathoner, C. Genovese, R. Arrigo, *Chem. Comm*. **2023**, *59*, 3005.
2. N. Mahmood, Y. Yao, J.-W. Zhang, L. Pan, X. Zhang, J.-J. Zou, *Adv. Sci*. **2018**, *5*, 1700464.
3. R. Nisticò, R. Mantovan, M. Cantoni, C. Rinaldi, M. Malandrino, S. Mostoni, M. D'Arienzo, B. Di Credico, R. Scotti, *J. Alloys Compd*. **2024**, *981*, 173628.
4. F. Germaninezhad, R. Hosseinzadeh, M. Tajbakhsh, A. Beitollahi, *Micro Nano Lett*. **2020**, *15*, 359.
5. S.A. Sarode, J.M. Bhojane, J.M. Nagarkar, *RSC Adv*. **2015**, *5*, 105353-105358.

Acknowledgements

This work received financial support from MUR (Italy) and the European Union – Next Generation EU, Mission 4, Component 1, CUP (H53D23004490001) through the PRIN Project MAPEC (N. 2022599NR3), and CUP (H53D23008000001) through the PRIN Project PERFECT (N. P2022TK9B9).

Catalytic behaviour of CuO and Co_3O_4 phases deposited on hollow @SiO_2 and @TiO_2 structures in toluene combustion

Anna ROKICIŃSKA[*,1], Magdalena ŻUROWSKA[1,2], Radosław SADOWSKI[1], Marek DĘBOSZ[1], Piotr ŁĄTKA[1], Piotr KUŚTROWSKI[1]

[1] *Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, Kraków, Poland*

[2] *Doctoral School of Exact and Natural Sciences, Jagiellonian University, Łojasiewicza 11, Kraków, Poland*

** anna.rokicinska@uj.edu.pl*

Significance and Relevance

Understanding the real role of interactions between typical components of a supported catalyst of volatile organic compounds (VOCs) combustion was possible by excluding additional parameters that could affect the catalytic behavior of the system (i.e. porosity, morphology and particle size of the support) due to the use of core-shell structures with controlled design. Special attention was paid to the study of the catalytic behavior of CuO and Co_3O_4 phases deposited on @SiO_2 and @TiO_2 spherical supports in toluene combustion.

Preferred and 2nd choice for the topic: Air cleaning and combustion, Automotive and stationary emission control (2nd choice)
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

VOCs are environmental pollutants recognized as substances causing photochemical smog, as well as carcinogenic and/or mutagenic effects in humans. Therefore, limiting the amount of VOCs released into the atmosphere is crucial for the protection of the environment and human health. A very promising method of controlling VOCs emissions is their catalytic combustion, but it requires the development of appropriately effective catalysts.[1] Particularly important in this context is a deeper understanding of the role of interactions between an active phase and a support, which can lead to improved catalytic properties in this reaction.[2] The dispersion and type of the active phase, as well as physicochemical properties of the support must be selected appropriately when designing catalysts, including novel core-shell materials. The advantage of the latter materials is not only the unique properties related to their nanometric structures, but also the arrangement of the individual components of the system that provides a well-controlled contact between the core and the shell.[1,3] The presented work focuses on the analysis of the catalytic behaviour of CuO and Co_3O_4 phase particles deposited on spherical @SiO_2 and @TiO_2 supports in the catalytic combustion of toluene. The use of supports with comparable particle size, morphology and porosity allowed to minimize the influence of diffusion effects and to expose the real role of the components of the studied systems and their interactions in the catalytic process.

Materials and Methods

The polymer templating method was used for the synthesis of the @SiO_2 and @TiO_2 supports. Oxide phase precursors were deposited on the surface of spherical particles of polystyrene or resorcinol-formaldehyde resin, respectively. Subsequently, the polymer@oxide composites were modified with Cu^{2+} or Co^{2+} cations using wet impregnation. The amounts of the introduced components were chosen to obtain 5, 10 and 15 wt.% of CuO or Co_3O_4 in the final catalyst. The synthesized materials after removal of the polymer core by high temperature calcination were examined using XRD, XRF, UV-Vis-DR, XPS, SEM/EDX, DRIFT and H_2-TPR. Moreover, their catalytic activity in the total oxidation of toluene was tested.

Results and Discussion

The TiO_2 and SiO_2 supports of similar morphology and porosity were synthesized in order to exclude the influence of these parameters on the catalytic activity of CuO and Co_3O_4 phases in the total

oxidation of toluene. The supports of uniform spherical shape with comparable BET surface area of 38 m^2/g and 29 m^2/g for @SiO_2 and @TiO_2, respectively, were obtained. Analysis of XRD patterns for these materials confirmed the presence of amorphous SiO_2 phase and TiO_2 in the anatase form. In the next step, the active phase was introduced by wet impregnation by depositing 5, 10 and 15% by mass of the appropriate oxide, respectively. XRD measurements for the catalysts containing Cu showed the formation of the CuO phase. In the case of the Co-containing materials, the Co_3O_4 phase was obtained only for the @SiO_2 support, while for the @TiO_2_Co catalysts, the $CoTiO_3$ phase additionally appeared beside the spinel phase. Similar observations were made based on the results of UV-Vis-DR measurements.

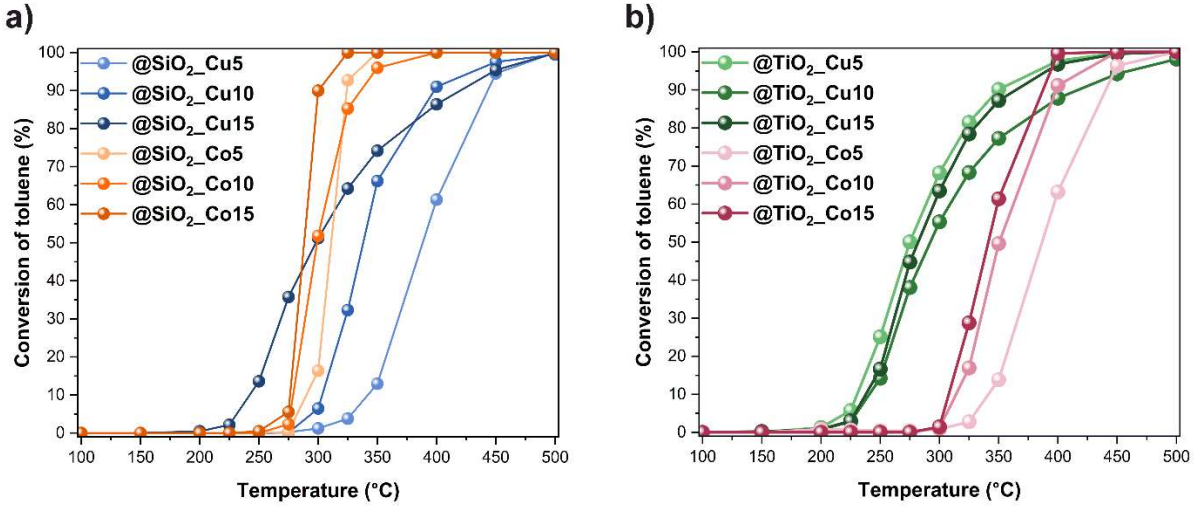


Figure 1. Catalytic activity of (a) @SiO_2- and (b) @TiO_2-based catalysts in total oxidation of toluene.

The synthesized materials were characterized by high catalytic activity in the process of total oxidation of toluene. Depending on the active phase - support system used, the catalytic properties of the studied materials change. The best activity was achieved over the @TiO_2_Cu and @SiO_2_Co catalysts. A stronger interaction of the cobalt oxide precursor with the @TiO_2 support resulted in the formation of the surface $CoTiO_3$ phase, which is more resistant to reduction than Co_3O_4. In turn, separate particles of Co_3O_4 phase were formed on the @SiO_2 support, which more easily participates in the reaction according to the Mars–van Krevelen mechanism. Additionally, it was observed that the presence of copper causes the catalysts to be active already at low reaction temperatures, achieving complete conversion at much higher temperatures than those containing cobalt. In the latter case, there is a small temperature difference from the onset temperature to the achievement of complete toluene conversion. It was found that the formation of the $CoTiO_3$ phase does not have a positive effect on the catalytic activity, causing deactivation of the catalyst in the tested process. On the other hand, the different dispersion of the CuO phase on the SiO_2 support also has an adverse effect on the catalytic performance.

References

1. A. Rokicińska, P. Łątka, B. Olszański, M. Żurowska, M. Dębosz, M. Michalik, P. Kuśtrowski, *Chemical Engineering Journal* **2024**, *480,* 148173.
2. R. Riva, H. Miessner, R. Vitali, G. Del Piero, *Applied Catalysis A: General* **2000**, *196*, 111-123
3. Z. Li, J. Hou, X. Gu, L. Gao, G. Su, F. Li, *Journal of Materials Science* **2022**, *57*, 4990-5005.

Acknowledgements

We thank the National Science Centre of Poland for financial support in the implementation of research (grant no. 2020/39/D/ST5/02703).

Electroprotic reactions of hydrogen peroxide at the interface of aqueous solution and the surface of amorphous oxide ZrO_2, Nb_2O_5, HfO_2, Ta_2O_5 gels – relevance for advanced oxidation processes

Kamila SOBAŃSKA,*[,1] Łukasz WOLSKI,[2] Piotr PIETRZYK[1]
[1]*Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, 30-387 Krakow, Poland.*
[2]*Adam Mickiewicz University, Faculty of Chemistry, Uniwersytetu Poznańskiego 8, 61-614 Poznań, Poland.*
**kamila.sobanska@uj.edu.pl*

Significance and Relevance

An electroprotic mechanism of the generation of reactive oxygen species (ROS) on amorphous non-redox oxides ZrO_2, Nb_2O_5, HfO_2, Ta_2O_5 has been developed. A change in reactivity of peroxidase type (formation of reactive oxygen species) to catalase one (formation of dioxygen, including singlet oxygen) depending on the pH of the solution has been shown. The electroprotic mechanism leads to the simultaneous formation of superoxide and hydroxyl radicals.

Preferred and 2nd choice for the topic: Water treatment and Fundamental advances in understanding catalysis
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Due to the increasing use of hydrogen peroxide (H_2O_2) as a cheap and environmentally benign oxidant in many catalytic reactions, extensive studies into mechanisms of H_2O_2 activation (decomposition), and the search for new catalysts active in this reaction have recently received much attention.[1] H_2O_2 is a simple source of reactive oxygen species (ROS) such as hydroxyl radicals, superoxide radicals, hydroperoxyl radicals, peroxide anions, or singlet oxygen. They can be used in advanced oxidation processes (AOP) and for catalytic wastewater treatment.[2,3]

In this contribution, we describe the application of amorphous oxide gels (ZrO_2, Nb_2O_5, HfO_2, Ta_2O_5) for profuse generation of ROS via H_2O_2 decomposition, by exploiting its pH-tunable peroxidase- and catalase-like reactivity. For this purpose, the influence of the isoelectric point, pH of the reaction mixture, and the crystallinity degree of the oxide catalysts on ROS formation and speciation was examined employing spin trapping and dissolved oxygen measurements, as well as the test reactions for peroxidase-like activity with OPD and NBT substrates. The results were accounted for by a new electroprotic mechanism of H_2O_2 activation, where an ionic sponge comportment of the gels plays a crucial role.

Results and Discussion

Investigation into the interaction of aqueous solutions of H_2O_2 with the surface of amorphous oxides of ZrO_2, Nb_2O_5, HfO_2, Ta_2O_5 led to the establishment and later generalization of the electroprotic mechanism of ROS formation. The reaction between amorphous gels and H_2O_2 in aqueous solution has been studied using EPR (HYSCORE), Raman, UV-Vis, FTIR, TG-MS, and XPS techniques over a wide range of pH and peroxide concentration. We identified various reaction intermediates, such as O_2^- and $^\bullet OH$ radicals, as well as O_2^{2-} peroxide groups (**Figure 1a,b,c**). Under acidic conditions, superoxide and hydroxyl radicals were generated simultaneously in large amounts, and their peak concentration was reached near the isoelectric point of the amorphous catalysts. In this pH region, the amorphous gels exhibited peroxidase-type activity, quantitatively measured by the o-phenylenediamine oxidation assay. Above the isoelectric point, O_2^{2-} formation (Raman observations) is accompanied by significant O_2 release due to catalase-like activity (**Figure 1d**). The role of electroprotic processes has been established based on pH dependence. The similar pattern of concentration profiles corresponding to O_2^- and $^\bullet OH$ suggests that both types of radicals are formed simultaneously during the decomposition of H_2O_2 according to the electroprotic mechanism: $\equiv M^+\text{-}HO_2^-{}_{(surf)} + H_2O_{2(aq)} \rightarrow {}^\bullet OH_{(aq)} + M^+\text{-}O_2^-{}_{(surf)} + H_2O$. The surface of the investigated amorphous oxides was covered with hydroxyl groups. These groups

control electrolytic equilibrium by exchanging and capturing charged intermediates of the electroprotic decomposition reaction of H_2O_2. This observation rules out the homolytic decomposition of hydrogen peroxide exclusively into •OH radicals postulated earlier.

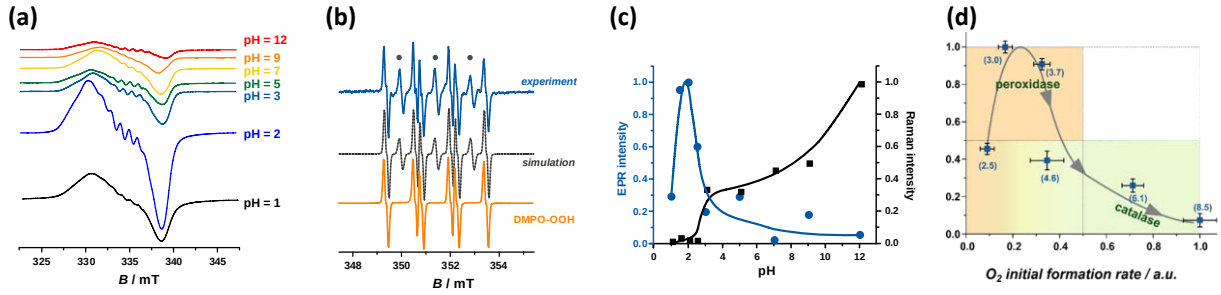


Figure 1 Identification of reactive oxygen species formed during the interaction of H_2O_2 with amorphous Nb_2O_5. (a) EPR spectra of the interaction of H_2O_2 with Nb_2O_5, (b) EPR spectra using DMPO spin trapping, (c) changes with pH in the EPR signal of superoxides and Raman signal of peroxides, (d) change in peroxidase and catalase type reactivity under pH.

The catalytic screening was carried out for the oxide gels (UV-vis, methylene blue (MB) degradation with H_2O_2). We carried out detailed catalytic studies for Nb_2O_5-based materials. The contribution of ROS generated *in situ* or *ex situ* to the elimination of ciprofloxacin (CIP) was evaluated. We tracked the kinetics of CIP removal by UV-vis spectroscopy, while identification of CIP degradation products was obtained by liquid chromatography-mass spectrometry (LC-MS). We found that surface O_2^{2-} and O_2^- groups significantly improved the adsorption efficiency of CIP on Nb_2O_5 by modifying the surface charge. At the same time, we showed that better removal of CIP in the dark and the presence of H_2O_2 was mainly determined by the adsorption process. We confirmed the enhanced adsorption by infrared (IR) spectroscopy, total organic carbon (TOC) measurements, and elemental analysis. We observed effective chemical degradation of adsorbed CIP after exposing the Nb_2O_5/H_2O_2 system to UV light. We further showed that niobium oxide is therefore a promising inorganic adsorbent that can be easily regenerated in an environmentally friendly manner by UV light exposure.

References

1. K. Sobańska, P. Pietrzyk, Z. Sojka, *ACS Catal.* **2017**, *7*, 2935.
2. L. Wolski, K. Sobańska, A. Walkowiak, K. Akhmetova, J. Gryboś, M. Frankowski, M. Ziolek, P. Pietrzyk, *J. Hazard. Mater.* **2021**, *415*, 125665.
3. Y. Deng, R. Zhao, *Curr. Pollution Rep.* **2015**, 1, 167.

Acknowledgments

This work was financially supported by the National Science Center, Poland (NCN), grant OPUS27 2024/53/B/ST4/03929.

The challenge of large-scale application of biomimetic photocatalytic water treatment

Jiaqiang Wang*, Yi Zhao, Die Zou, Han Zhang, Chenjie Duan
Yunnan Provincial Center of Technology Innovation for New Materials and Equipment in Water Pollution Control, School of Materials and Energy, School of Chemical Sciences & Technology, Yunnan Province Engineering Research Center of Photocatalytic Treatment of Industrial Wastewater, Yunnan University, Kunming, 650091, P. R. China .
** e-mail jqwang@ynu.edu.cn*

Significance and Relevance

Very limited studies on full-scale photocatalytic treatment of wastewater are available in the literature, fact that renders difficult the large-scale application in spite of numerous research articles on the application of heterogeneous photocatalysis.1 On the other hand, biotemplating is an effective strategy to obtain morphology controllable materials with structural specialty, complexity, and related unique properties. Biotemplating is also readily available at low costs and on a large scale. 2
This presentation will summarize the recent advances in the synthesis of nano/microstructures using biotemplates. Particularly, the design, assembling, and manufacturing of a few novel skid-mounted plug flow photocatalytic reactors will be reported. The applications in the treatment of hospital wastewater, lignite gasification wastewater, wastewater at the expressway service area, and hydropower stations will also presented. Finally, the future challenges and opportunities for photocatalytic wastewater treatment will be discussed

Introduction and Motivations

At present, there are few reviews on the preparation of photocatalytic materials by biological templates and their practical applications. On the other hand, very limited studies on full-scale photocatalytic treatment of wastewater are available in the literature, fact that renders difficult the large-scale application in spite of numerous research articles. More importantly, this could be one of the first commercial photocatalytic reactors presented so far. It would be also expected that more people will be attracted to do further study about skid-mounted plug flow photocatalytic reactors treatment of wastewater.

References

1. S. K. Loeb, et al., *Environ. Sci. Technol*. 2019, 53, 2937.
2. X. Ma, et al., *Catal. Sci. Technol*. 2024, 2024, 14, 10.
3. J. Wang in UV-Visible Photocatalysis for Clean Energy Production and Pollution Remediation: Materials, Reaction Mechanisms, and Applications, Chapter 20 (Eds.:X Wang, M Anpo, X Fu), Wiley-VCH GmbH, 2023, pp. 285–294.

Hydrogen spillover on a non-reducible metal oxide comprising earth-abundant elements and its catalysis

Kazuki SHUN[1], Kohsuke MORI[*,1], Takumi KIDAWARA[1], Hiromi YAMASHITA[1]
[1] *Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka Suita Osaka 565-0871, Japan*
**mori@mat.eng.osaka-u.ac.jp*

Significance and Relevance

Hydrogen spillover, the simultaneous diffusion of protons (H^+) and electrons (e^-), were firstly achieved on a non-reducible MgO with heteroatom Al dopants (Al-MgO). This material exhibited more than 3 times larger of H^+ capacity compared with reducible metal oxides comprising rare elements, even though it is composed of only earth-abundant elements. Moreover, the spilled hydrogen on Al-MgO promoted the catalysis of Ni during CO_2 hydrogenation by a factor of 4.6. This work provides a new strategy for designing functional materials intended to hydrogen spillover for diverse application.

Introduction and Motivations

Hydrogen spillover, the simultaneous diffusion of protons (H^+) and electrons (e^-), is considered to be applicable to ubiquitous technologies related to hydrogen but limited to over reducible metal oxides composed of rare elements.[1, 2] The present work demonstrates that a non-reducible MgO with heteroatom Al dopants (Al-MgO) allows hydrogen spillover in the same way as reducible metal oxides. Furthermore, a H^+ storage capacity of this materials owing to hydrogen spillover is more than three times greater than those of various standard metal oxides based on H^+ transport channels within its bulk region. Atomic hydrogen diffuses over the non-reducible Al-MgO produces active H^+-e^- pairs, as also occurs on reducible metal oxides, to enhance the catalytic performance of Ni during CO_2 hydrogenation. The H^+ and e^- diffusion pathways generated by the heteroatom Al doping is disentangled based on systematic characterizations and calculations.

Materials and Methods

$Mg(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ were firstly dissolved in distilled water. This solution was dropped to aqueous solution of Na_2CO_3 and NaOH and stirred overnight. Obtained white slurry was washed and dried. The resulting solid was calcined under air atmosphere for 1.25 h at 400 °C to obtain Al-MgO. Ru nanoparticles were deposited onto Al-MgO by the impregnation of $RuCl_3{\cdot}nH_2O$ and following hydrogen reduction to yield Ru/Al-MgO (Ru = 2 wt%, Mg/Al=5). Ru/MgO was prepared in the same manner as Ru/Al-MgO.

Results and Discussion

The hydrogen spillover property of Al-MgO was comprehensively evaluated from the viewpoint of the H^+ diffusion ability and e^- diffusion ability. In order to the evaluate the H^+ diffusion ability of Al-MgO, thermogravimetry measurements under H_2-D_2 switching atmosphere were exhibited for Ru/MgO and Ru/Al-MgO, respectively. In response to switching between H_2 and D_2 flowing at 400 °C, the weight of Ru/Al-MgO rapidly changed compared with that of Ru/MgO (**Figure 1 (a)**). From these results, the H^+ storage for Al-MgO was calculated to be 0.29 wt%, more than 3 times larger than that of various reducible metal oxide as well as MgO (**Figure 1 (a)**). A combination of *in situ* DRIFT and mass spectrometry under H_2-D_2 switching atmosphere revealed that H^+ can diffuse both onto the surface and into the bulk of Al-MgO that extremely enhance the H^+ storage of Al-MgO although it can migrate only onto the surface of MgO. In order to evaluate the e^- diffusion ability of Al-MgO, *in situ* UV-vis measurement under H_2 heating atmosphere was performed for the mixture of WO_3 and Ru/Al-MgO. As the results, WO_3 mixed with Ru/Al-MgO specifically absorbed visible light due to the mixed valence state of W^{5+} and W^{6+} over 200 °C indicating that e^- diffusion over Al-MgO (**Figure1 (b)**). These results show that both of H^+ and e^- diffusions were facilitated over non-reducible MgO by the addition of Al,

even though Mg^{2+} and Al^{3+} are both originally irreducible. The pathways of enhanced H^+ and e^- diffusion on Al-MgO was further studied by systematic characterizations and calculations.

Hydrogen spillover on the Al-MgO was utilized for the promotion of catalytic CO_2 hydrogenation on Ni. The CO_2 conversion of Ni/Al-MgO increased by a factor of 4.6 by the physical mixture with Pt/Al-MgO, the initiator of hydrogen spillover. *In situ* XAFS measurements during H_2-O_2 switching atmosphere elucidated the acceleration of the Ni reduction under the presence of Pt (**Figure2 (a)**). Therefore, the hydrogen spillover on Al-MgO readily removed poisoning oxygen on Ni evolved by CO_2 activation to enable effective catalysis during CO_2 hydrogenation (**Figure2 (b)**).

This material offers the design of functional materials based on hydrogen spillover as well as catalysts applicable to the ubiquitous hydrogen handling technologies for upcoming hydrogen society.[3]

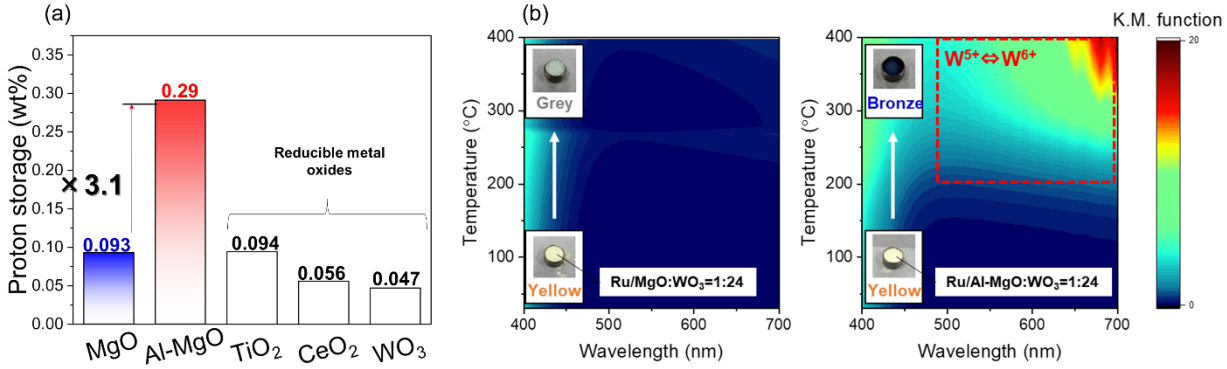


Figure 1 Characterizations describing the enhanced H^+/e^- diffusion over Al-MgO.
(a) The weight transition of Ru/MgO and Ru/Al-MgO under a H_2-D_2 switching atmosphere. (b) The transition in visible light absorption of WO_3 mixed with Ru supported each sample.

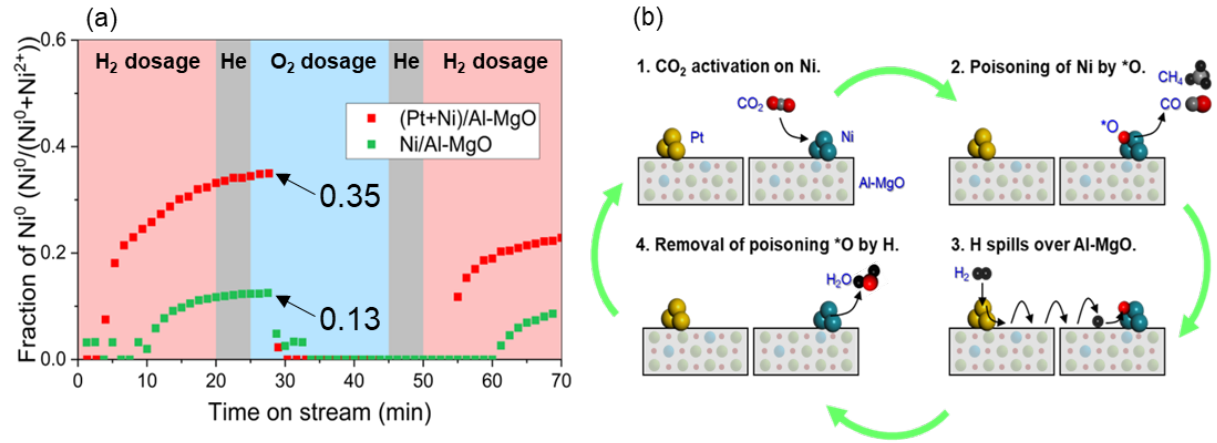


Figure 2 How hydrogen spillover on Al-MgO endows CO_2 hydrogenation on Ni.
(a) The fraction of metallic Ni^0 species in the (Pt + Ni)/Al-MgO, Ni/Al-Mg based on linear fitting for Ni K edge XANES at 350 °C. (b) A schematic diagram illustrating how hydrogen spillover on Al-MgO promotes the catalysis of Ni in CO_2 hydrogenation.

References

1. R. Prins, *Chem. Rev.* **2012**, *5*, 2714-2738.
2. W. Karim, C. Spreafico, A. Kleibert, J. Gobrecht, J. VandeVondele, Y. Ekinci, J. A. van Bokhoven, *Nature* **2017**, *541*, 68-71.
3. K. Shun, K. Mori, T. Kidawara, S. Ichikawa, H. Yamashita, *Nat. Commun.* **2024**, *1*, 6403.

STACY: International collaboration towards liquefied hydrogen safety

Hirohisa TANAKA[*, 1], Ernst Arndt REINECKE[2], Nabiha CHAUMEIX[3], Ahmed BENTAIB[4], Daiju MATSUMURA[5], Masashi TANIGUCHI[6], Shannon KRENZ[2], Tomohito NAKAYAMA[1], Shinya UEGAKI[1], Itsuki JINJO[1], Seita KURONO[1]

[1] *Kwansei Gakuin University, 1 Gakuen-Uegahara, Sanda, Hyogo 669-1330, Japan*

[2] *Forschungszentrum Jülich GmbH (FZJ), 52425 Jülich, Germany*

[3] *Centre National de la Recherche Scientifique (CNRS), Orléans, France.*

[4] *Institut de Radioprotection et de Sûreté Nucléaire (IRSN), Fontenay-aux-Roses, France.*

[5] *Japan Atomic Energy Agency, SPring-8, 1-1-1 Koto, Sayo, Hyogo 679-5148, Japan*

[6] *Daihatsu Motor Co., Ltd., 21-1 Momozono, Ikeda, Osaka 563-8651 Japan*

** e-mail corresponding: hirohisa.tanaka@kwansei.ac.jp*

Significance and Relevance

Liquefied hydrogen has three characteristics compared to gases in the event of a leak: (1) cryogenic temperatures, (2) high expansion and low oxygen concentration, and (3) high energy density. A passive autocatalytic recombiner (PAR) to ensure the safety requires (1) improved low-temperature activity, (2) enhanced response, (3) suppression of spontaneous ignition, and additionally (4) robustness against surface contamination. A brand-new PAR was designed by devising the crystal structure of a new catalyst at the atomic level, prototyping the actual catalyst in a laboratory, and conducting repeated reaction experiments using various equipment, including large high-pressure vessels.

Preferred choice for the topic:	*H_2 storage and transportation, green H_2 production, hydrogen vectors*
2nd choice for the topic:	*Sustainable and clean energy production and transport*
Preferred presentation:	*Oral only / Oral preferred*

Introduction and Motivations

Global efforts aim to decarbonize the energy sector by increasing the share of renewable energies in the energy mix. Energy storage technologies are needed to store surplus energy generated from fluctuating energy sources and make it accessible when needed. In this context, large-scale storage and transportation of liquefied (cryogenic) hydrogen (LH2), which has a high storage density, is expected to play a fundamental role in a potential hydrogen economy of the future.

To realize the economic benefits and societal acceptance of LH2, an international research collaboration between Germany, France and Japan has been working since 2022 on the development of technologies that contribute to the safety of the storage and transportation of liquefied hydrogen. The project name is "Towards the safe storage and transportation of cryogenic hydrogen" and the acronym is "STACY". The results of three years of research are summarized here.

Results and Discussion

Powder catalysts with various chemical compositions such as Pd/Al_2O_3, Pt/Al_2O_3, $Pt/CeZrYO_{2-\delta}$, and $CaZrPtO_3$ were prepared, and oxidation and reduction pretreatments were compared to explore the effect of different surface conditions on cryogenic catalytic activity [1-2]. In particular, differences in the mechanisms of hydrogen oxidation activity of various catalysts at sub-zero temperatures were investigated using isotope of oxygen. Furthermore, catalysts coated on honeycomb supports with various cell densities were prepared, and the effect of hydrogen concentration on the hydrogen oxidation reaction rate was clarified (Figure 1).

Coanfig. No.	#900	#100	#30	#7	#3
Cell Configuration					
Cell density / cell cm^{-2}	139.5	15.5	4.4	1.1	0.5
Cell (hole) size / cm	0.08	0.25	0.45	0.91	1.43
Note	900 cell·inch^{-2}	100 cell·inch^{-2}	30 cell·inch^{-2}	4-cell holes of #30	9-cell hole of #30

Figure 1. Configuration of honeycomb-type catalysts

The catalytic reactivity can be controlled to the desired value by the cell configuration. It was shown that reducing the cell density can generate natural convection for the oxidation of hydrogen accumulated in a closed space, improving the amount of hydrogen oxidation (Figure 2) [3-4].

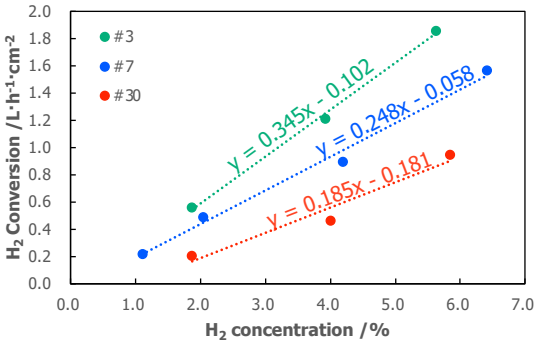


Figure 2. H_2 conversion rate by natural convection using exothermic H_2 oxidation reaction

On the other hand, there is a concern that if high-concentration hydrogen is oxidized all at once, the exothermic reaction may exceed the hydrogen auto-ignition temperature. To mitigate the sudden heat generation, the concept of multi-stage catalysts was investigated, and its effectiveness was experimentally confirmed. It was also shown that Pt-Fe/CZY can selectively catalyze hydrogen at room temperature in the presence of CO, a catalyst poison that inhibits catalytic reactions [5]. Thus, a comprehensive guideline for catalyst design as a PAR in the event of an LH2 leak has been compiled.

References

1. Nishihata, Y., Mizuki, J., Akao, T., Tanaka, H., Uenishi, M., Kimura, M., Okamoto, T., Hamada, N., Self-regeneration of a Pd-perovskite catalyst for automotive emissions control, *Nature*, 418, p.164-167 (2002). DOI: 10.1038/nature00893
2. Tanaka, H., Taniguchi, M., Uenishi, M., Kajita, N., Tan, I., Nishihata, Y., Mizuki, J., Narita, K., Kimura, M., Kaneko, K., Self-regenerating Rh- and Pt-based perovskite catalysts for automotive-emissions control, *Angew. Chem. Int. Ed.*, 45, p.5998-6002 (2006). DOI: 10.1002/anie.200503938
3. Reinecke, E.-A., Takenaka, K., Ono, H., Kita, T., Taniguchi, M., Nishihata, Y., Hino, R., Tanaka, H., Performance tests of catalysts for the safe conversion of hydrogen inside the nuclear waste containers in Fukushima Daiichi, *Inter. Jour. of Hydrogen Energy*, 46 p.12511-12521 (2021). DOI: 0.1016/j.ijhydene.2020.08.262
4. Ono, H., Takenaka, K., Kita, T., Taniguchi, M., Matsumura, D., Nishihata, Y., Hino, R., Reinecke, E-A., Takase, K., Tanaka, H., Research on hydrogen safety technology utilizing the automotive catalyst, *E-Journal of Advanced Maintenance*, Vol.11, No.1, p.40-45 (2019). ISSN-1883-9894/10
5. Inagawa, K., Matsumura, D., Taniguchi, M., Uegaki, S., Nakayama, T., Urano, J., Aotani, T., Tanaka, H., Development of hydrogen oxidation reaction catalysts to overcome CO poisoning and elucidation of reaction mechanism, *J. Phys. Chem. C*, 127, p.11542−11549 (2023). DOI: 10.1021/acs.jpcc.3c02237

Acknowledgements

This work was the results of the international joint project “Towards Safe Storage and Transportation of Cryogenic Hydrogen (STACY)” supported by International Collaborative Research Program of the “EIG CONCERT-Japan”; the German Federal Ministry of Education and Research under Grant No. 01DR22007, the French Government under Grant No. ANR-22-HTCE-0003-02, and the Japan Science and Technology Agency (JST), under Grant No. JPMJSC21C3, Japan.

The synchrotron radiation experiments were performed at BL14B1 in SPring-8 under the approval of Japan Synchrotron Radiation Research Institute (Proposal No. 2022A3609, 2022B3609, 2022B3630, 2023A3630, 2023B3630, 2024A3609, 2024B3631). The SPring-8 experiment was also supported by the Advanced Research Infrastructure for Materials and Nanotechnology in Japan (ARIM Japan) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan (Grant No. JPMXP1222AE0023, JPMXP1223AE0003, JPMXP1223AE0019) and the Shared-Use Program of JAEA Facilities (Proposal No. 2022B-E05, 2023A-E03, 2023B-E02, 2024B-E14)

Deactivation and kinetic models of catalytic methane pyrolysis over Fe/Al_2O_3 catalysts for a fluidized bed reactor integrated system

Piercosimo VEDELE[1*], Enrico SARTORETTI[1], Fabio SALOMONE[1], Massimiliano ANTONINI[2], Samir BENSAID[1]
[1]*Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129, Turin, Italy.*
[2] *Hysytech srl, Via I Maggio 5, 10043, Orbassano, Italy.*
**piercosimo.vedele@polito.it*

Significance and Relevance

The research explores catalytic methane pyrolysis as a sustainable hydrogen production method, focusing on the development of a fluidized bed reactor (FBR) associated with a regeneration section. Iron-based catalysts were synthesized through Wet Impregnation (WI) and Solution Combustion Synthesis (SCS) and were subjected to several characterization techniques. SCS catalysts, which show enhanced performance, were chosen for in-depth deactivation and kinetic studies and were involved in an innovative and flexible dynamic model enabling a precise FBR integrated system simulation under changing operational parameters.

Preferred topic: H_2 storage and transportation, green H_2 production, hydrogen vectors;
2nd choice for the topic: Catalysis to electrify the chemical production.
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Fossil fuel combustion drives high pollutant emissions, urging alternative solutions. Hydrogen production emerges as a crucial pathway in the research of a sustainable energy transition. The primary methods for hydrogen production include Steam Methane Reforming (SMR), coal gasification, and water electrolysis. SMR and gasification are the most widely used and low-cost methods but involve significant environmental impact. In contrast, electrolysis powered by renewable sources offers low emissions but incurs high production costs and is highly susceptible to climatic variability. Consequently, there is a critical need to develop economically viable methods for fossil fuel utilization with reduced carbon footprints. Catalytic methane pyrolysis stands out as a promising technology, decomposing methane into solid carbon and "turquoise hydrogen" via catalytic action[1]. This study investigates the catalytic performance of various iron-based catalysts with a focus on deactivation and kinetic models and designs a fluidized bed reactor (FBR) integrated system for methane pyrolysis.

Materials and Methods

Various synthesis techniques, i.e. Wet Impregnation (WI) and Solution Combustion Synthesis (SCS), were employed to produce iron-alumina catalysts with specific iron loadings (40 wt% – 60 wt% Fe_2O_3) and distinct textural properties. Several characterization methods (ICP-MS, H_2-TPR, XRD, BET, Raman, FESEM, TEM, EDX) were employed to assess the structure, composition, and morphology of the synthesized samples. Time-On-Stream (TOS) and kinetic analyses were conducted to determine the catalysts activity, stability, and kinetic parameters (reaction order and activation energy). A dynamic MATLAB model was developed, also taking into account thermodynamic equilibrium and time-dependent mass transfer limitations.

Results and Discussion

The catalytic performances were examined in correlation with structural and morphological properties. XRD and Raman spectroscopy analyses revealed the presence of α-Fe_2O_3 in all the fresh samples. Despite their lower specific surface area, SCS catalysts exhibited smaller iron crystallites (Table 1). Instead, the impregnated samples preserve part of the high surface area characteristic of the initial alumina. Iron-oxides reduction is needed to produce metallic iron, the methane pyrolysis active site. SCS catalysts maintain smaller iron-crystallite size than WI, indicating a higher resistance to sintering phenomena. During the pyrolysis reaction, active sites undergo a transformation to iron

carbide (Fe_3C) due to carbon formation. TEM and EDX show the production of high-quality carbon (CNTs) and a good dispersion of iron active sites over the alumina matrix (Figure 1a, b). The study examined catalytic activity and kinetics under various conditions, showing that SCS samples have superior activity due to effective iron dispersion. Kinetic analysis provided key parameters, including reaction order (ca. 1 for all the samples), pre-exponential factor, and activation energy (Table 1). Deactivation tests at different temperatures provided parameters to develop an activity model for the SCS catalyst (Figure 1c). These deactivation and kinetic models were involved in the design of a fluidized bed reactor integrated with a separation section[3] in which the carbon product is recovered from the spent catalyst; the partially regenerated catalyst is then cycled back to the reactor, in a continuous closed loop. The performances of the FBR were predicted, evaluating how the global yield of the process and the fluidization depend on reaction conditions and separation efficiencies.

The reactor modeling study allowed to clearly identify the optimal process parameters for maximizing the production of turquoise hydrogen and high-quality carbon. This research highlights an innovative system for greenhouse gas reduction in the hydrogen production sector, in the context of an increasingly necessary energy transition.

Table 1. Textural and kinetic properties of some of the Fe/Al_2O_3 materials (60 wt% Fe_2O_3).

Sample	S_{BET} / m^2 g^{-1}	Pore size / nm	Crystal size / nm	E_{act} / kJ mol^{-1}
Fe/Al_2O_3 – SCS (fresh)	46.5	0.11	29	-
Fe/Al_2O_3 – WI (fresh)	91.8	0.18	55	-
Fe/Al_2O_3 – SCS (reduced)	16.9	0.27	49	133
Fe/Al_2O_3 – WI (reduced)	45.2	0.09	139	160

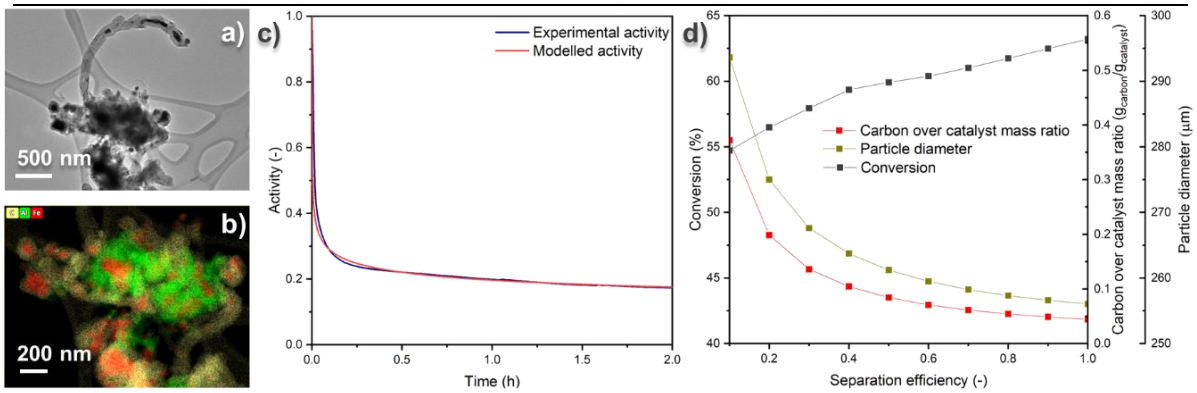


Figure 1. TEM (a) and EDX (b) images of spent Fe/Al_2O_3 - SCS; SCS catalyst experimental activity profile vs modeled activity profile (c); methane conversion, carbon over catalyst mass ratio and particle diameter at different separation efficiencies for a fluidized bed reactor simulated at 700 °C in an integrated system (d).

References

1. N. Sánchez-Bastardo et al., Methane pyrolysis for zero-emission hydrogen production: A potential bridge technology from fossil fuels to a renewable and sustainable hydrogen economy, Industrial & Engineering Chemistry Research, 60 (2021) 11655.
2. D. Kunii, O. Levenspiel, Fluidization Engineering, Butterworth-Heinemann, 1991.
3. S. Schneider et al., State of the Art of Hydrogen Production via Pyrolysis of Natural Gas, ChemBioEng Reviews 7.5 (2020), 150-158.

Acknowledgements

The authors gratefully acknowledge the support of AGRITECH for providing resources and funding during the research activity. The REACT-EU program PON Ricerca e Innovazione 2014-2020 (D.M. 1062/2021) and the Italian Ministry of University and Research (MUR) are kindly acknowledged.

Machine learning analysis of halide perovskite for photocatalytic CO_2 reduction and water splitting

Beyza YILMAZ, Ramazan YILDIRIM*
Boğaziçi University, Department of Chemical Engineering, 34342, Istanbul, Türkiye.
yildirra@bogazici.edu.tr

Significance and Relevance

Halide perovskites, well-known for their exceptional optical and electrical characteristics, have proven effective as light absorbers in solar cells. Similarly, these features such as strong light absorption, flexible bandgap tuning, and excellent charge transport are also crucial for photocatalytic applications. This research applies machine learning tools to explore how these properties can be leveraged to enhance the efficiency of CO_2 reduction and hydrogen evolution through photocatalysis. Random forest models were developed to predict the bandgap of perovskites and product formation rates considering the structure and properties halide perovskite as well as reaction conditions as the descriptors (input variables).

Preferred and 2nd choice for the topic: Preferred: Photocatalysis and Photoelectrocatalytic approaches, Solar Energy Utilization; 2nd: CO_2 utilization and recycling
Preferred presentation: Oral

Introduction and Motivations

Increasing environmental concerns have significantly boosted the demand for renewable and sustainable energy sources in recent years.[1,2] Harnessing solar energy and transforming it into alternative forms, such as chemical energy by producing solar fuels like hydrogen, methane or methanol, offers a promising strategy to address energy needs.[1] For instance, photocatalytic H_2 evolution is considered as sustainable and environmentally friendly process for generation of hydrogen fuel.[3,4] Similarly, photocatalytic CO_2 reduction (ie. artificial photosynthesis) is a novel way to produce valuable chemicals like hydrogen, carbon monoxide, methane, and methanol utilizing water and undesired CO_2.[1,5] These photocatalytic reactions require effective photocatalysts that can be activated by solar illumination and are stable within reaction conditions during processes.[5]

Halide perovskites, represented by the formula ABX_3 (where A and B are cations and X is a halide anion) have gained great attention as semiconductors due to their revolutionary performances in photovoltaics in last two decades. Although they could not be initially used for photocatalytic applications due to their inherent instability under humid conditions, this has changed with recent developments to improve their stability while their unique chemical structures allow for the easy tuning of properties like bandgap, light absorption efficiency, charge carrier mobility, and diffusion length to optimize photocatalytic performance.[1,6] Various halide perovskite materials with tailored properties have been developed experimentally for CO_2 reduction and H_2 evolution reactions, resulting in a significant body of research in the literature.

This study aims to gather insights on photocatalytic CO_2 reduction and H_2 evolution over halide perovskites from existing literature, compile a comprehensive dataset, and evaluate it via machine learning techniques. Key trends and influential factors were identified to create predictive models for the bandgap of halide perovskites, CO_2 reduction and H_2 evolution rates.

Materials and Methods

Photocatalysis over halide perovskites has been investigated in the literature for years between 2017 and 2024. The dataset was established using 115 articles on CO_2 reduction and 62 papers on H_2 evolution using the details of experimental conditions and recorded performance. Information on the

structure of halide perovskites, their synthesis methods, cocatalysts, cocatalyst deposition methods, reaction conditions, illumination details were used as descriptors while the total product formation rate was taken as the output variable. Photocatalytic CO_2 reduction and H_2 evolution reactions handled separately; however, all the perovskites used as photocatalysts in the dataset were examined together. The dataset was analyzed using descriptive statistics and machine learning methods to identify important variables and patterns, which were subsequently used to predict the perovskite bandgap, CO_2 reduction and H_2 evolution rates (expressed in terms of total product formation rate). The power of predictive models was assessed according to their root mean squared error and r-squared values. The relative importance of descriptors was also analyzed using The SHAP (SHapley Additive exPlanations) analysis.

Results and Discussion

The dataset was first analyzed using simple descriptive statistic to understand the major trends and identify the important descriptors for the predictive models. Then, a predictive model for the bandgap of perovskites were constructed first to compute its missing values in the dataset and computed values, together with the experimental bandgaps, were used (as one of the main descriptors) for the predictive models for CO_2 reduction and H_2 evolution processes. Figure 1 shows the prediction results of random forest models developed for the bandgap of halide perovskites and total product formation rate for CO_2 reduction; the models successfully predicted both bandgap of perovskites with RMSE of 0.12 (R^2=0.92) and the CO_2 reduction with RMSE of 0.33 (R^2=0.91). Analysis showed that the chemical components of perovskites were highly influential for photocatalytic performance, and hot injection was the most common perovskite synthesis method.

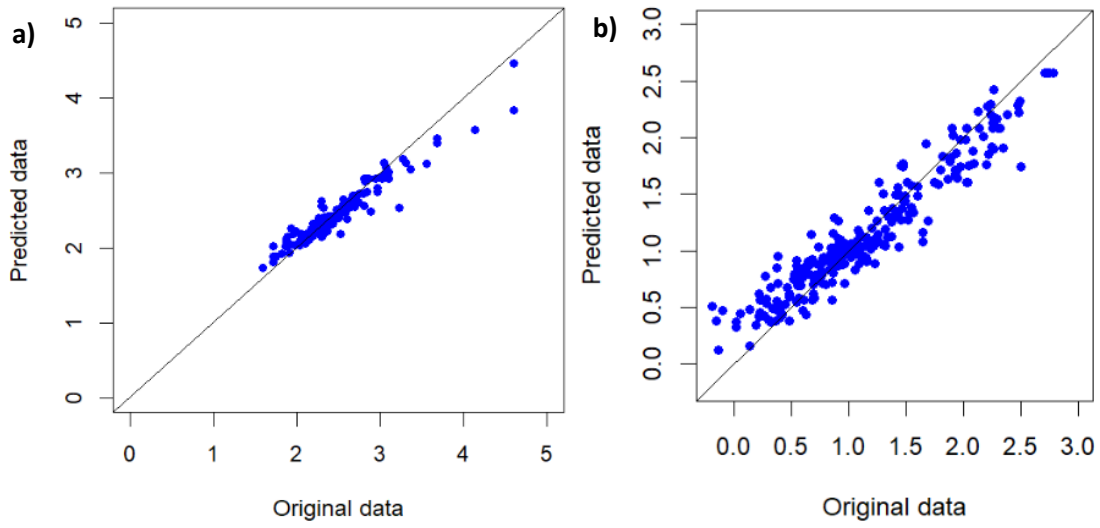


Figure 1 Results of random forest prediction models for a) bandgap b) total gas production rate.

References

1. K. Bienkowski, R. Solarska, *ACS Catal.* **2024**, *9*, 6603-6622.
2. B. Yılmaz, B. Oral, R. Yıldırım, *IJHEDX* **2023**, *48*, 24904-24914.
3. E. Can, R. Yıldırım, *Appl. Catal. B: Environ.* **2019**, *242*, 267-283.
4. S.A. Ali, T. Ahmad, *Mater. Today Chem.* **2023**, *29*, 101387.
5. CH.Tan, *Front Energy Res* **2022**, 9, 1-7.
6. B. Yılmaz, Ç. Odabaşı, R. Yıldırım, *Energy Technol.* **2022**, *10*, 2100928.

Acknowledgements

This work was financially supported by Boğaziçi University Research Fund through Project No: 19950

Magnetic field-enhanced electrochemical oxygen evolution reaction using $Co_3O_4/BaFe_{12}O_{19}$ co-catalyst system

Dorottya Szalay[1], Amy Radford[1], Chen Wu[2], Shik Chi Edman Tsang[1]*
[1] *Wolfson Catalysis Centre, Department of Chemistry, University of Oxford, Oxford, OX1 3QR, United Kingdom*
[2] *School of Materials Science and Engineering, State Key Laboratory of Silicon and Advanced Semiconductor Materials, Zhejiang University, Hangzhou 310027, China*
* edman.tsang@chem.ox.ac.uk

Introduction

In order to help reduce the effects of global warming and climate change, lot of scientific attention has been put towards finding a clean fuel source. Hydrogen stands out as an idea; option due to its high energy density (143 MJ/kg, which is three times that of liquid hydrocarbons) and its combustion byproduct, water, making it a zero-carbon emission energy source. [1] However, hydrogen production remains largely dependent on non-renewable sources. Most hydrogen is generated through coal gasification and steam-methane reforming, while a more sustainable method—electrocatalytic water splitting—accounts for only 3-5% of hydrogen production due to its high energy requirements. [2] This water-splitting process involves two half-reactions: the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), with the latter posing a significant bottleneck. OER is a complex, four-electron process that demands high overpotentials, leading to slow reaction kinetics. [3]

This research investigates the use of Co_3O_4 electrocatalysts with $BaFe_{12}O_{19}$ magnetic co-catalysts as a highly efficient system for electrochemical OER. Research has shown that OER is a spin-related electron transfer where controlling the spins of intermediate oxygen radicals can result in more efficient production of triplet molecular oxygen. [4] This project aims to take advantage of the magnetic properties of barium ferrite and combine them with stable and corrosive-resistant cobalt oxide to create improved OER electrocatalysts under applied external magnetic fields.

Results and Discussion

Five different systems were investigated: pure Co_3O_4, pure $BaFe_{12}O_{19}$ mixed $Co_3O_4/BaFe_{12}O_{19}$ with ratios of 1:0.5, 1:1 and 1:1.5, keeping the amount of active Co_3O_4 catalyst constant. Chronoamperometry measurements with magnetic pulses at 2 V vs RHE were conducted to evaluate the catalytic properties of these systems and to investigate the effects of applied magnetic fields at various strengths (200 mT, 400 mT and 800 mT) and results are shown on Figure 1a. Increasing the amount of barium ferrite results in lower current densities, as it decreases the exposed electrochemically active surface area of cobalt oxide. However, the relative magnitude of the magnetic effect increases up to the 1:1 ratio sample, then decreases as the amount of active catalyst becomes less than that of the co-catalyst (Figure 1b). Therefore, with a focus on spin-pinning, this research investigates the combined effects of spin-pinning, magnetohydrodynamics and Lorentz forces to better understand how external magnetic fields can enhance electrochemical water splitting.

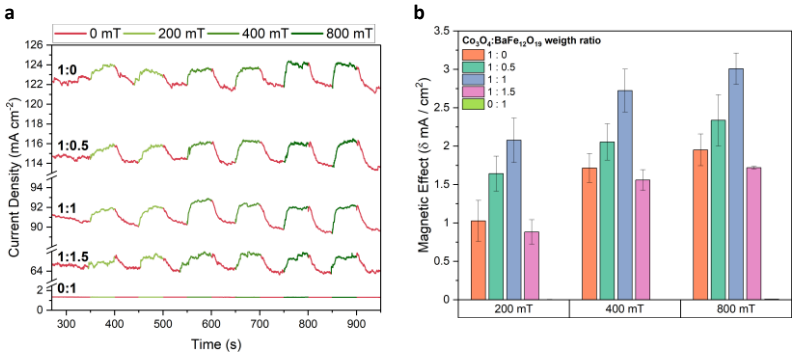


Figure 1. a) . Pulsed magneto-chronoamperometry results of the 5 systems with magnetic pulses: 200 mT (light green), 400 mT (medium green) and 800 mT (dark green). Note that barium hexaferrite shows no catalytic activity. b) Size of magnetic effect in chronoamperometry tests.

Significance

This project examines the impact of an externally applied magnetic field on electrochemical reactions, a rapidly growing area in chemistry with substantial gaps in the existing literature. This study delves into the fundamental chemical principles underlying magneto-electrochemistry and expands the experimental framework by investigating the use of a magnetic co-catalyst to enhance electrochemical activity of OER.

Materials and Methods

Cobalt oxide was synthesized through a two-step method. Barium hexaferrite was synthesized *via* a sol-gel method. Resulting powder samples were characterized by PXRD and SQUID. Catalyst materials were suspended in ethanol with 5% Nafion binding agent and drop-casted onto carbon paper. These were used in a standard 3-electrode system with Hg/HgO reference electrode and Pt counter electrode in 1 M KOH. Pulsed magneto-chronoamperometry measurements were recorded at constant potentials and are presented here with reference to the reversible hydrogen electrode (vs RHE). External magnetic field was applied using an electromagnet.

References

1. K. Mazloomi and C. Gomes, Renewable Sustainable Energy Rev., **2012**, *16*, 3024-3033.
2. Y. Liu, D. Zhou, T. Deng, G. He, A. Chen, X. Sun, Y. Yang and P. Miao, ChemSusChem, **2021**, *14*, 5359-5383.
3. J. Lim, S. Yang, C. Kim, C.-W. Roh, Y. Kwon, Y.-T. Kim and H. Lee, Chem. Commun., **2016**, *52*, 5641-5644.
4. T. Wu, X. Ren, Y. Sun, S. Sun, G. Xian, G. G. Scherer, A. C. Fisher, D. Mandler, J. W. Ager, A. Grimaud, J. Wang, C. Shen, H. Yang, J. Gracia, H.-J. Gao and Z. J. Xu, Nat. Commun., **2021**, *12*, 3634.

Spontaneous Adsorption of Iridium Chloride Complex on oxychloride photocatalysts Provides Efficient and Durable Reaction Site for Photocatalytic Water Oxidation

Hajime SUZUKI,[1] Kengo MINAMIMOTO,[1] Yusuke ISHII,[1] Osamu TOMITA,[1] Akinobu NAKADA,[1] Shunsuke NOZAWA,[2] Ryu ABE*,[1]

[1]*Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan*

[2]*Photon Factory (PF), Institute of Materials Structure Science (IMSS), High Energy Accelerator Research Organization (KEK), Tsukuba, Ibaraki 305-0801, Japan*

** ryu-abe@scl.kyoto-u.ac.jp*

Significance and Relevance

Sillén(-Aurivillius)-type layered oxyhalides, such as Bi_4NbO_8Cl, have been reported to function as stable O_2-evolution photocatalysts in Z-scheme water splitting systems. While investigating effective cocatalysts and their loading methods to enhance O_2 evolution on the representative oxychloride photocatalyst Bi_4NbO_8Cl, we discovered for the first time that highly dispersed $IrO_xH_yCl_z$ species, spontaneously formed by simply stirring Bi_4NbO_8Cl particles in an aqueous Na_3IrCl_6 solution in dark, significantly enhanced the O_2 evolution rate. Moreover, this novel adsorption method proved effective for various oxyhalide photocatalysts.

Preferred and 2nd choice for the topic: "Photocatalysis and photoelectrocatalytic approaches, solar energy utilization" preferred or "H_2 storage and transportation, green H_2 production, hydrogen vectors"
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Sillén(-Aurivillius)-type layered oxyhalides (e.g., oxychlorides) such as Bi_4NbO_8Cl have emerged as promising photocatalysts for visible-light-driven water splitting (Figure 1).[1] Along with exploring related oxyhalide materials, their synthetic methods such as flux-assisted synthesis have been studied to improve their photocatalytic activities.[2] On the other hand, there is still plenty room for exploring their surface engineering, such as loading effective cocatalysts for water oxidation.

Results and Discussion

The oxyhalide photocatalyst Bi_4NbO_8Cl was synthesized using the flux method previously reported.[2] The loading of IrO_2 cocatalysts was carried out via various methods such as the colloidal adsorption (COL), microwave-assisted (MW) method, and photodeposition (PD) method, all of which have been reported as effective for loading IrO_2 on metal oxide and oxynitride photocatalysts.[3-5] Note that, the PD method was proposed to provide IrO_2 species through the oxidation of a Ir precursor $Ir^{III}Cl_6^{3-}$ to $Ir^{IV}O_2$ by photogenerated holes on the photocatalyst accompanied by the reduction of nitrate ions (e.g., $NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + 2H_2O$) by photoexcited electrons.[5] In addition to the above methods, herein we introduced a simple adsorption (ADS) method, which was originally carried out as one of the control tests of the above mentioned PD method. In particular, the photocatalyst particles were just suspended in an aqueous Na_3IrCl_6 solution (in the absence of NO_3^-) in dark.

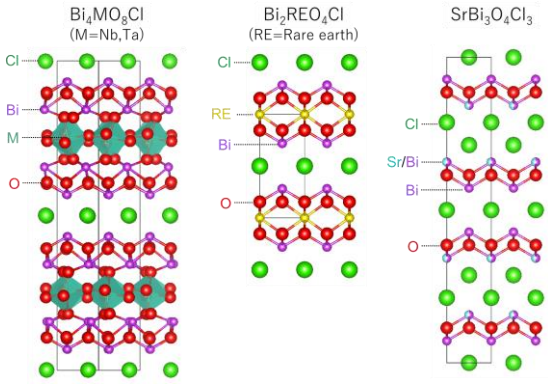


Figure 1 Crystal structures of layered oxyhalide photocatalysts: Bi_4MO_8Cl (M=Nb, Ta), Bi_2REO_4Cl (RE=Rare Earth), and $SrBi_3O_4Cl_3$.

Figure 2 shows the O_2 evolution rates on each Bi_4NbO_8Cl sample (0.1 g) in an aqueous $AgNO_3$ solution (8 mM, 100 mL) under visible light irradiation ($\lambda > 400$ nm) from a 300-W Xe-arc lamp. The PD

method afforded higher rate than IMP, whereas COL and MW ones resulted in slightly higher than bare one but much lower than IMP. Surprisingly, newly attempted ADS method provided almost same rate to PD one, in other words, the highest O_2 evolution rate.

The loaded Ir species via APD were characterized using multiple techniques. ICP measurements indicated that most of the Ir species introduced (0.5 wt% as metal) were successfully loaded on the surface of Bi_4NbO_8Cl, regardless of the loading methods. STEM observations of ADS one showed that identifying the Ir species is nearly impossible. This suggests that the ADS method successfully deposited highly dispersed Ir species on the surface, likely in the form of extremely small particles or cluster-like structures. In the EXAFS spectra (Figure 3), the Ir species loaded by the COL, MW, and IMP methods show only Ir-O bond in the first coordination shell, suggesting that the Ir species exist as oxides or hydroxides. In contrast, the Ir-loaded samples prepared by the ADS and PD methods exhibit not only Ir-O bond but also the bond attributed to Ir-Cl, strongly suggesting that Ir species represented as $IrO_xH_yCl_z$ contributed to the enhanced O_2 evolution.

We applied this novel ADS method to other oxychloride photocatalysts: Bi_4TaO_8Cl, Bi_2ErO_4Cl, and $SrBi_3O_4Cl_3$ (Figure 1). Figure 4 shows the O_2 evolution rates for the oxyhalide photocatalysts onto which Ir species were loaded using the ADS method. The O_2 evolution rates were significantly improved by loading Ir species for both Sillén-type (Bi_2ErO_4Cl, and $SrBi_3O_4Cl_3$) and Sillén-Aurivillius-type (Bi_4NbO_8Cl and Bi_4TaO_8Cl) oxychlorides. As demonstrated above, the novel ADS method was found for the first time to be a mild, simple, and versatile method for loading active and stable Ir species that can significantly enhance the O_2 evolution rates on various oxychlorides photocatalysts.

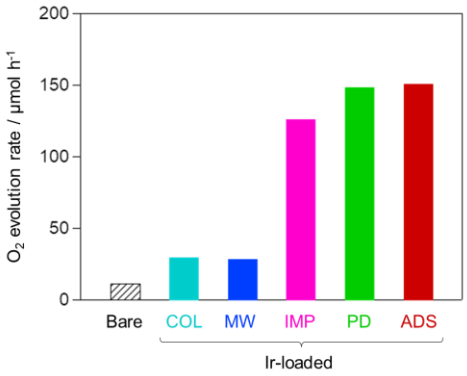


Figure 2. Initial O_2 evolution rate of Bi_4NbO_8Cl loaded with Ir species *via* various methods.

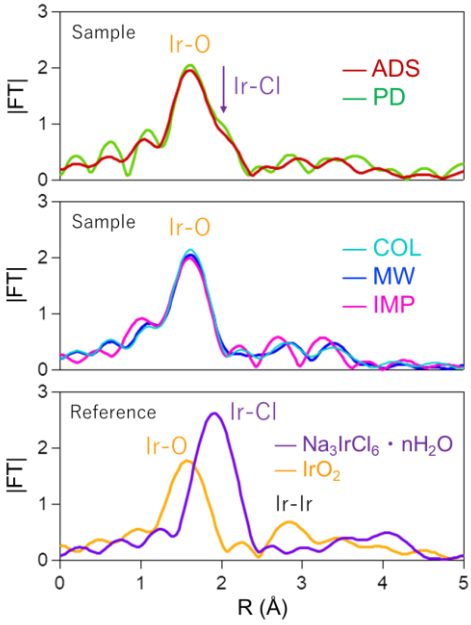


Figure 3. Fourier-transformed Ir L3-edge EXAFS spectra of Bi_4NbO_8Cl loaded with Ir species *via* various methods.

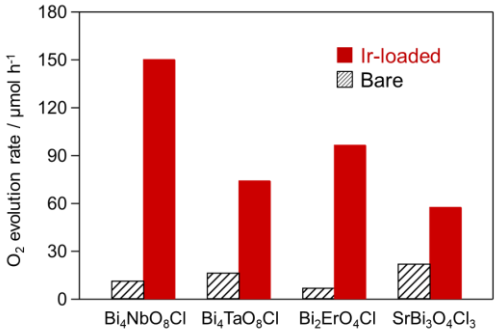


Figure 4. Initial O_2 evolution rate of oxyhalides loaded with or without Ir species *via* adsorption (ADS) method.

References

1. D. Kato, H. Suzuki, R. Abe, H. Kageyama, *Chem. Sci.* **2024**, *15*, 11719-11736.
2. K. Ogawa, R. Abe, et. al. *ACS Appl. Mater. Interfaces* **2019**, *11*, 5642-5650.
3. Maeda, K. Domen, K. *Angew. Chem. Int. Ed.* **2012**, *51*, 9865-9869.
4. K. Chen, J. Xiao, K. Domen, et. al. *J. Am. Chem. Soc.* **2023,** *145*, 3839-3843.
5. Iwase, A.; Kato, H.; Kudo, A. *Chem. Lett.* **2005**, *34*, 946-947.

Acknowledgements

This work was supported by the JSPS KAKENHI Grant Numbers JP20H00398, JP23H02061, and JP24KJ1470, and the JSPS Core-to-Core Program (JPJSCCA20200004).

Evaluation of Cu- and CuZn-Exsolved Catalysts for the CO_2 Hydrogenation to MeOH

Eleonora CALÌ[1*], Saman NOROOZI[1], William Skinner[2], David J. Payne[2,3], Fabio Salomone[1], Samir Bensaid[1]
[1]*Dept. of Applied Science and Technology, Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129 Turin, Italy.*
[2] *Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, U.K.*
[3] *NEOM Education, Research, and Innovation Foundation, Al Khuraybah, Tabuk 49643-9136, Saudi Arabia*
* *eleonora.cali@polito.it*

Significance and Relevance

Developing highly active and stable methanol synthesis catalysts is essential for transitioning from CO to CO_2 as carbon source in industrial applications promoting greener decarbonisation solutions. In this work, novel CO_2-to-methanol catalysts have been developed through the *exsolution* approach and benchmarked against the state-of-the-art commercial material. The new materials showed extremely high stability to deactivation and coarsening, as well as the dual formation of MeOH and DME, highlighting their potential as new generation catalysts for the CO_2 hydrogenation to MeOH reaction.
Preferred and 2nd choice for the topic: CO_2 utilization and recycling
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Among the most promising approaches to reduce CO_2 emissions through chemical valorization strategies, the CO_2 catalytic conversion to methanol (MeOH), a widely usable component for fuels, plastic, paints, chemicals, and a building block for more complex fuels, is considered an extremely promising strategy. Despite the growing interest in its industrial implementation, a major challenge related to this process is the low CO_2 conversion, triggered by limited catalyst selectivity and deactivation by active metal nanoparticle (NP) sintering. Recent works on materials improvement for efficient, stable and selective hydrogenation of CO_2 to MeOH have highlighted Cu-and-ZnO-based catalysts as among the most promising materials for this application.[1,2] However, even considering the state-of-the-art $Cu/ZnO/Al_2O_3$ commercial catalyst, problems arise from i) kinetic limitations when using CO_2 instead of CO as feed, ii) Cu instability, given its high mobility and proneness to sintering in operating conditions, and iii) low CO_2/H_2O tolerance.[3] The design of new catalysts with improved activity and stability is, hence, a key ambition in the field. In this work, the development of optimised catalysts for CO_2 conversion to MeOH using the novel approach of 'exsolution'[4] has been carried out. To obtain this, a solid solution incorporating Cu as ion into the 'host' structure was synthesised, followed by the *in situ* formation of surface metallic nanoparticles (NPs) through controlled reduction. After such NP exsolution, the samples were tested at relevant conditions for the CO_2 hydrogenation to MeOH to assess the newly developed catalysts' stability, activity and selectivity.

Materials and Methods

Spinel pure-phase materials were prepared by co-precipitation of nitrate precursors ($Zn(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$) in an NH_3 solution, followed by product separation and drying, and then calcined and sintered in air (T=700-850 °C). The exsolution of the as-synthesised samples was investigated in 5% H_2/N_2 at temperatures ranging between 350-550 °C and times between 4-10 h. Catalytic tests were carried out in a fixed-bed reactor at 23 barg pressure and temperatures ranging from 180-300 °C. To rationalise the catalytic performance of the different materials, all samples (pre- and post-exsolution and post-catalytic testing) were characterised by N_2 physisorption, XRD, H_2-TPR, CO_2-TPD, XPS, SEM, TEM, and STEM-EDX spectroscopy.

Results and Discussion

Characterisation of specific surface area (BET), affinity for CO_2 (CO_2 TPD), and surface species obtained (XPS) allowed to identify the best candidates for the investigated reaction before testing at operating pressure (23 barg) in the test rig. The results showed successful exsolution of both Cu-metal only and CuZn-alloy NPs after reduction at different conditions of temperatures, times, and humidity. The main differences among the investigated samples were found in the size of the exsolved NPs and the amount

of depleted dopant, mainly dependent on the reduction time. Instead, the reduction temperatures chosen determined the NPs' composition, with lower T being responsible for single-metal exsolution, as opposed to alloy exsolution at higher T, for the same starting composition. For all investigated samples, the exsolution strategy, thanks to the strong anchorage of the exsolved NPs to the spinel ($CuZnAl_2O_4$) host and the strain imposed by the NPs at the support interface by their unique "socketing" (*i.e.*, anchorage), maximised the Cu/CuZn-spinel interaction and stabilised the NPs on the surface of the oxide support, even after ~50 h of testing ($3H_2$:CO_2, 20 Nl/h, 23 barg, 180-300 °C). A maximum CO_2 conversion of ~17% was achieved for the best-performing samples, very close to the calculated thermodynamic equilibrium (Fig. 1a). When compared to the commercial catalyst ($Cu/ZnO/Al_2O_3$), the exsolved samples showed a much higher space-time yield (STY, $mmol_{MeOH}\ g_{Cu}^{-1}\ h^{-1}$), as shown in Figure 1b. Interestingly, dimethyl ether (DME) was detected as reaction product for all samples, as well as MeOH and CO, with the highest selectivity towards MeOH obtained at 200 °C (76%), as reported in Figure 1c. All the exsolved samples showed enhanced stability, with post-catalytic test characterisation showing no sintering/coalescence of the exsolved NPs, as demonstrated by the STEM-EDX comparison in Figure 1 d-e for the same sample pre- and post-catalytic testing, respectively.

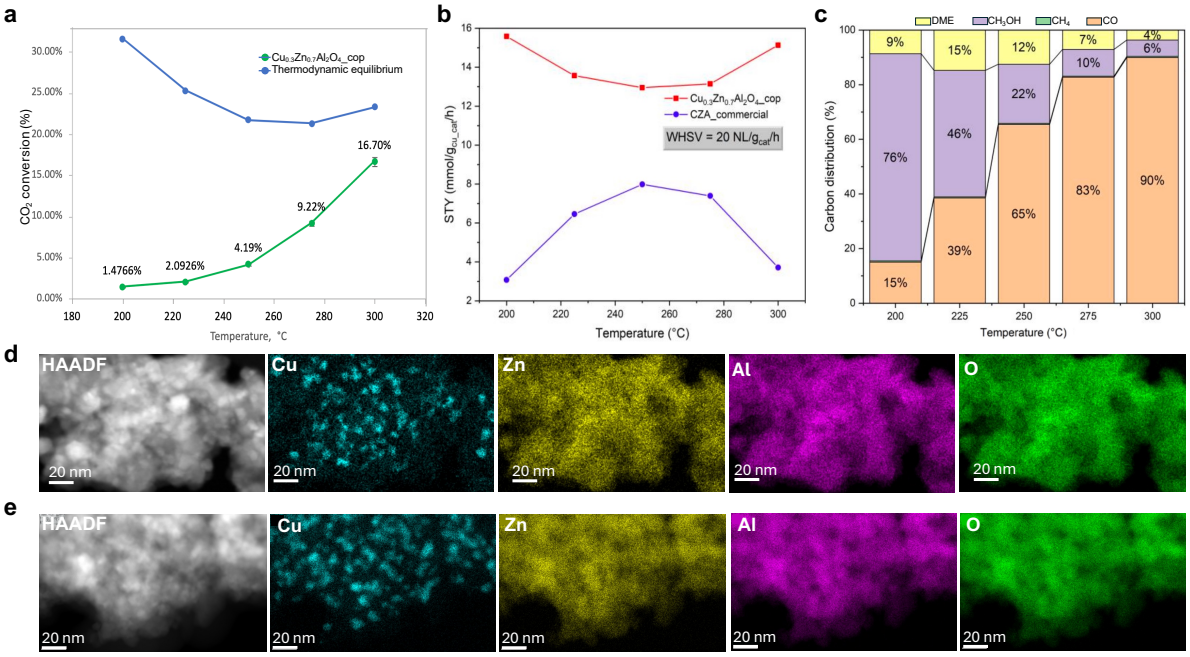


Figure 1. a) CO_2 conversion of the best performing exsolved spinel sample showing ~17% conversion at 300 °C; b) STY comparison for the best performing exsolved sample *vs.* the commercial $Cu/ZnO/Al_2O_3$ catalyst; c) product distribution obtained for tests at T=200-300 °C with DME production at all temperatures; d) STEM-EDX characterisation of an exsolved $Cu_{0.3}Zn_{0.7}Al_2O_4$ catalyst before and d) after ~50 h of continuous testing (T=200-300 °C; P= 23 barg) showing high stability of the exsolved NPs which retained their size and density distribution.

Building upon proven compositions of state-of-the-art catalysts, this work highlights the potential of new exsolved catalysts for the efficient catalytic CO_2 hydrogenation to MeOH. Specifically, the results obtained in this work open the possibility of overcoming some of the challenges hindering the implementation of such catalytic processes at industrial level, potentially advancing the technology of MeOH synthesis catalysts through achieving high activity *and* stability.

References

1. T. A. Atsbha, *et al.*, *J. CO_2 Util.* **2021**, 44, 101413.
2. Y. Liu, *et al.*, *ACS Catal.* **2024**, 14, 12610−12622.
3. S. Navarro-Jaen, *et al.*, *Nat. Rev. Chem.* **2021**, 5, 564.
4. Calì, E., *et al.*, *Nature Commun.* **2023**, 14(1), 1754.

Acknowledgements

This project has received funding from the EU HORIZON EUROPE research and innovation programme under the Marie Skłodowska-Curie grant agreement No: 101063146 (MEXCAT).

Confined growth of ultrasmall NiO nanoparticles into mesostructured and mesoporous SiO_2, γ-Al_2O_3 and CeO_2 supports for CO_2 methanation

Fausto Secci[1,2*], Nicoletta Rusta[1,2], Luciano Atzori[1,2], Maria Giorgia Cutrufello[1,2], Daniela Meloni[1], Carla Cannas[1,2], Elisabetta Rombi[1,2]

[1]*Department of Chemical and Geological Sciences, University of Cagliari, Monserrato (CA), Italy*

[2]*National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence, Italy*

**fausto.secci@unica.it*

Significance and Relevance

Different NiO- and NiO/CeO_2-based composite catalysts for CO_2 methanation were first obtained by dispersing the active phase into the pores of mesostructured SiO_2 (SBA-15). Particularly, two different impregnation methods, never applied to methanation catalysts to the best of our knowledge, were used, leading to catalysts with a different dispersion of NiO nanoparticles, featuring different catalytic activity. The presence of CeO_2 showed a significant promoting activity and, in this context, different Ni/Ce ratios were studied. Furthermore, other chemically different mesostructured/mesoporous supports (i.e. Al_2O_3 and CeO_2) were studied.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling (preferred); Circular economy (second choice)

Preferred presentation: Oral preferred, Short Oral as second choice

Introduction and Motivations

Due to the increasing attention toward global warming, current research is focusing on green fuels obtained by the reduction of captured CO_2 (e-fuels) with hydrogen obtained from renewable energy sources (green hydrogen). A prominent example of these e-fuels is methane, that is obtained from CO_2 through a reduction reaction called the "Sabatier reaction". Ni-based catalysts are currently among the most investigated systems for CO_2 methanation, due to their high activity and selectivity at relatively low temperatures and due to their low cost compared to catalysts based on noble metals [1,2]. Ni is often paired with a support/promoter, like CeO_2 or Al_2O_3. In this work, composite catalysts consisting of a NiO and NiO/CeO_2 active phase dispersed on mesostructured silica (SBA-15), mesostructured γ-Al_2O_3, and mesoporous CeO_2 are presented. The use of mesoporous/mesostructured supports should allow to obtain a high dispersion of NiO in form of small nanoparticles, leading to a good catalytic activity with a reduced amount of active phase. Chemically different supports have also been studied to determine their effect of the catalytic performance of the catalysts.

Materials and Methods

To obtain NiO- and NiO/CeO_2-based nanocomposites two different impregnation approaches were used: a two-solvent (TS) impregnation and an impregnation based on a self-combustion (SC) reaction. SBA-15 was used as support. NiO-based catalysts (NiO@SBA-15) were obtained with a weight loading of 4.5%; NiO/CeO_2-based ones (NiO/CeO_2@SBA-15) were obtained with the same NiO loading, using a 1:1 Ni:Ce molar ratio (total weight loading = 15%). The total weight loading of 15% was then maintained to study different Ni/Ce molar ratios, ranging from 1/1 to 4/1. To rule out any possible activity of CeO_2, CeO_2-based catalysts were synthesized with a CeO_2 loading of 10.5%. Mesostructured γ-Al_2O_3 and mesoporous CeO_2 were subsequently used as supports to host NiO with a weight loading of 4.5%. To determine their structural, textural, and morphological properties, the catalysts were characterized with both small-angle (SA-) and wide-angle (WA-) XRD (X-ray diffraction), TEM (transmission electron microscopy), and nitrogen physisorption; they were also characterized with TPR (temperature-programmed reduction) and tested for CO_2 methanation.

Results and Discussion

WA-XRD show that the composites obtained with the SC impregnation do not feature any diffraction peak, suggesting that NiO and CeO_2 are deposited into the mesopores as ultra-small nanoparticles. On the other hand, the composites obtained with the TS impregnation show broad but visible crystal reflections attributed to both NiO and CeO_2, indicating that the active phase has crystallized forming larger nanoparticles. This finding is also confirmed by TEM micrographs, which, for SC composites, do not show the presence of any visible particle attributable to the active phase outside the mesopores; TS systems, conversely, visibly show darker nanoparticles dispersed over the support.

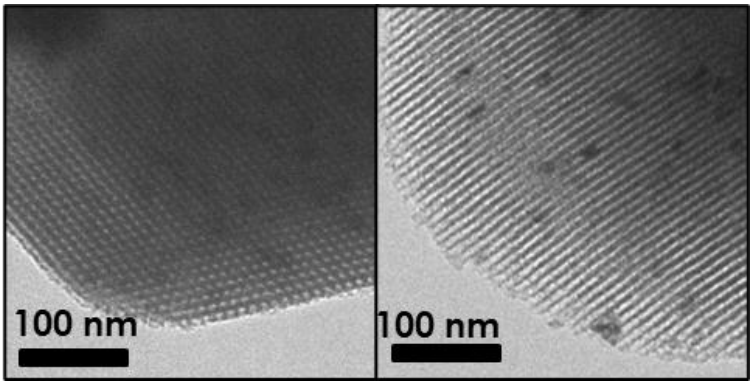


Figure 1 TEM micrographs of two NiO/CeO_2@SBA-15 composites obtained with SC (left) and TS impregnation (right).

The catalytic tests show a significantly positive effect of CeO_2 as promoter on performances in terms of CO_2 conversion (X CO_2 = 19% for NiO@SBA-15_SC vs. 48% for NiO/CeO_2@SBA-15_SC); furthermore, the catalysts obtained with the SC impregnation show a higher CO_2 conversion (X CO_2 = 48% for NiO/CeO_2@SBA-15_SC vs. 38% for NiO/CeO_2@SBA-15_TS), presumably due to the higher dispersion of active phase obtained with this approach. The Ni/Ce ratio, studied on 15 wt% composites obtained with the SC method, also shows a remarkable effect on the performance, with the 2/1 ratio featuring better performances than the 1:1 ratio. The effect of the different support (mesostructured γ-Al_2O_3 and mesoporous CeO_2) on the catalytic behavior, was also investigated.

References

1. W.J. Lee, *et al*. *Catalysis Today,* **2021**, 368, 2-19.
2. M.A.A. Aziz *et al*. *Green Chemistry,* **2015**, 17, 2647-2663.

Acknowledgements

This work has been developed within the framework of the project e.INS- Ecosystem of Innovation for Next Generation Sardinia (cod. ECS 00000038) funded by the Italian Ministry for Research and Education (MUR) under the National Recovery and Resilience Plan (NRRP) - MISSION 4 COMPONENT 2, "From research to business" INVESTMENT 1.5, "Creation and strengthening of Ecosystems of innovation" and construction of "Territorial R&D Leaders".

Optimizing Ni-Based Catalysts for Dry Reforming of Methane: Impact of MgO Supports Doped with Fe, Cu, and Ce

L. VALENTINO*[,1], G. PANTALEO[1], V. LA PAROLA[1], L.F. LIOTTA[1]

[1] *Institute for the Study of Nanostructured Materials (ISMN), National Research Council (CNR), Via Ugo La Malfa 153, 90146 Palermo, Italy.*

** lauravalentino@cnr.it*

Significance and Relevance

This study explores the improvement of Ni-based catalysts supported on MgO and doped with Fe, Cu and Ce, focusing on the improvement of stability and catalytic efficiency in the dry reforming of methane (DRM). Comprehensive chemical and physical characterizations reveal a strong relationship between catalyst structural properties, activity and carbon deposition resistance, providing valuable insights to optimize syngas production and promote DRM as a sustainable fuel generation process.

Preferred and 2nd choice for the topic: Sustainable and clean energy production and transport/CO_2 utilization and recycling
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Dry reforming of methane is an effective catalytic process for converting two significant greenhouse gases, methane (CH_4) and carbon dioxide (CO_2), into syngas (a mixture of CO and H_2), which serves as a valuable feedstock for synthetic fuels. This process not only offers a pathway for sustainable energy production but also addresses environmental challenges by mitigating greenhouse gas emissions.[1] Ni-based catalysts are commonly used for DRM due to their cost-effectiveness and high activity in CH_4 activation; however, their long-term stability is compromised by issues like carbon deposition, sintering, and deactivation at high temperatures. Improving the structural and chemical properties of the support can enhance the catalyst stability and reduce coke formation.[2,3] In particular, this study investigates the role of magnesium oxide and MgO doped with metals such as Fe, Cu, and Ce in promoting catalyst durability and efficiency, with the goal of improving the applicability of DRM for sustainable syngas production (Figure 1).

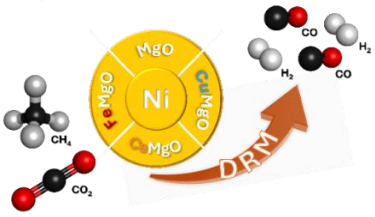


Figure 1. Schematic representation of the DRM reaction carried out over Nickel catalysts supported on MgO and MgO doped with Fe, Cu and Ce.

Materials and Methods

Ni catalysts were supported on MgO and MgO doped with Fe, Cu, and Ce. The supports were synthesized via hydrothermal precipitation and then calcined at 600 °C. Ni was deposited onto the prepared magnesium oxide supports through wetness impregnation, followed by calcination at 600 °C. Before the DRM reaction, an in-situ reduction was performed at 800 °C for 1 hour under an H_2/Ar atmosphere. DRM reaction was carried out in a fixed-bed reactor by feeding a gas mixture of CH_4 and CO_2 (ratio 1:1). Catalytic performance in DRM was evaluated, and post-reaction characterization, including XRD and TGA-DSC, was carried out to investigate structural stability and carbon deposition behavior.

Results and Discussion

The influence of dopants on the reduction properties, structural phase composition and on the catalytic activity was investigated. Comparison of the catalytic performance of Ni-MgO catalysts, shown in Figure 2, with CH_4 and CO_2 conversion curves plotted against temperature, demonstrates the activity of these catalysts in DRM. All samples display strong overall catalytic performance. In the temperature range of 450–700 °C, the conversion of the reactants follows the trend Ni-FeMgO < Ni-CuMgO < Ni-MgO < Ni-CeMgO. The lower conversion observed with the Fe-doped catalyst is probably due to side reactions, such as the reverse water-gas shift, for which Fe-based catalysts are highly active. Above 700 °C, CH_4 and CO_2 conversions reach approximately 90% and 100%, respectively, for the Ni-MgO catalysts.

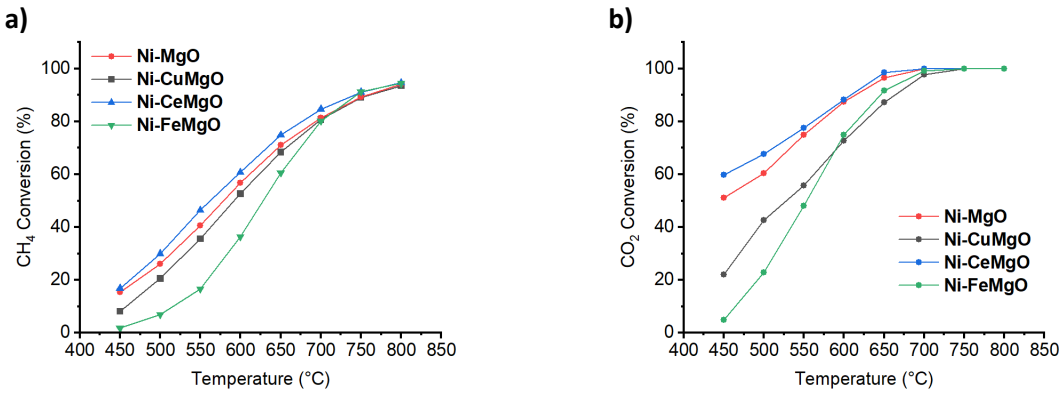


Figure 2. DRM results of Ni-MgO catalysts as a function a) CH_4 and b) CO_2 Conversion vs Temperature at 450–800 °C.

Characterization of the catalysts using XRD and TGA-DSC after the DRM reaction provided insights into structural stability, coke formation, and decomposition temperatures. These results offer valuable guidelines for optimizing Ni-based catalysts for sustainable syngas production, contributing to the broader application of DRM in environmental and energy solutions.

References

1. X. Cai, Y.H. Hu, *Energy Sci Eng.* **2019**, *7*, 4–29.
2. V. La Parola, L. F. Liotta, G. Pantaleo, M. L. Testa, A. M. Venezia, *Appl. Catal.A: Gen.* **2022**, *642*, 118704.
3. Huang, Y. Yan, S. Saqline, W. Liu, B. Liu, *Appl. Catal. B: Environ.* **2020**, *275*, 119109A.

Acknowledgements

The project “Investimento 3.5 “Ricerca e sviluppo sull’idrogeno” - Missione 2 “Rivoluzione verde e transizione ecologica” – Componente 2 “Energia rinnovabile, idrogeno, rete e mobilità sostenibile” previsto nell’ambito del Piano Nazionale di Ripresa e Resilienza (PNRR), di cui al Decreto MITE n. 545 del 23/12/2021, Progetto “Ricerca e sviluppo di tecnologie per la filiera dell’idrogeno (POR H2)”, CUP: B93C22000630006” is acknowledged for financial support.

A combined *operando* UV-vis and flow reactor study of the NH_3-SCR redox kinetics over Cu-CHA

C. Negri[1], N. Usberti[1], G. Contaldo[1], M. Bracconi[1], I. Nova[1], M. Maestri[1*], E. Tronconi[1*]
[1]*Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, 20156 Milano (Italy)*
**Corresponding authors: matteo.maestri@polimi.it; enrico.tronconi@polimi.it*

Significance and Relevance

This study highlights the accessibility of extracting kinetically relevant data directly from spectroscopy. Specifically, we employ *operando* UV-Vis Diffuse Reflectance spectroscopy coupled with a packed bed flow reactor to extract quantitative kinetic information on Cu^{II}/Cu^{I} redox dynamics during the NH_3-Selective Catalytic Reduction (SCR) on Cu-CHA catalyst. We quantified the fraction of Cu^{II} by Multivariate Curve Resolution (MCR) while simultaneously monitoring the gas-phase evolution during the reaction. These data enabled the univocal estimation of apparent rate parameters, demonstrating that combined analysis of UV-Vis spectra and gas-phase dynamics provides kinetic insight able to shed new light on catalytic pathways.

Preferred and 2nd choice for the topic: Fundamental advances in understanding catalysis; Automotive and stationary emission control
Preferred presentation: Oral preferred

Introduction and Motivations

A primary challenge in catalytic kinetics is to get direct insights on the catalytic cycle, that is crucial to derive mechanistic kinetic models and to optimize both catalysts and processes. In this context, simultaneously monitoring both gas phase species and the catalyst sites can provide an invaluable set of information. Herein we exemplify this concept in the case of the Selective Catalytic Reduction with ammonia (NH_3-SCR) redox chemistry over Cu-exchanged chabazite zeolites (Cu-CHA).

NH_3-SCR on Cu-CHA catalysts is the state-of-the-art technology to abate NO_x emissions from lean burn heavy-duty vehicles and passenger cars. The catalytic activity is associated with a Cu redox cycle. In the Reduction Half Cycle (RHC), Cu^{II} is reduced to Cu^{I}, releasing N_2 and H_2O, and in the Oxidation Half Cycle (OHC) Cu^{I} is re-oxidized to Cu^{II} with O_2 and H_2O. Notwithstanding many in-depth studies about Cu speciation and reaction intermediates during the two redox half-cycles, the NH_3-SCR mechanism over Cu-CHA is still lively debated in the literature. A crucial step regards the role played by binuclear Cu intermediates [1-2], with a longstanding debate in the literature regarding the RHC kinetic dependence on Cu^{II} (first versus second order rate).[1,4] It appears clear that the direct and contemporary measure of the evolution of Cu oxidation state and of the gas phase composition would provide valuable data to discriminate these proposals. In this work, we employ UV-Vis *operando* spectroscopy to monitor the Cu^{II}/Cu^{I} redox dynamics during the NH_3-SCR RHC and OHC, while measuring in parallel the outlet NO and N_2 concentration transients to assess the gas-phase reaction kinetics. This approach aims at simultaneously extracting kinetic insights while acquiring relevant spectroscopic data. This approach allows for combined studies of heterogeneous catalysts, targeting a deeper understanding of the reaction mechanism and quantification of the kinetic, elucidating the nuclearity of the active sites and their evolution over time.

Materials and Methods

The *operando* UV-Vis spectra are measured with an *ad hoc* setup developed in-house specifically designed to extract kinetically relevant information, coupling a packed bed microreactor with a high temperature UV–Vis diffuse reflectance probe [3]. The Cu-CHA catalyst (Si/Al_2O_3 ratio = 25, Cu = 1.77 wt%) has been pelletized, chopped and sieved (75 - 106 µm fraction), loading the quartz reactor with 64 mg of powders (total amount of Cu in the sample = 17.8 µmol), diluted with 66 mg of cordierite. The temperature is controlled by a thermocouple placed in close contact with the catalytic bed. The outlet concentrations of NO, NO_2, NH_3 are continuously monitored by an on-line ABB LIMAS analyser.

Kinetic measurements are carried out under isothermal conditions in the low temperature range (150-220°C), with protocols addressing the RHC (100 Ncc/min, 1000 ppm NO, 1000 ppm NH_3 / He balanced and 2%H_2O) and the OHC (100 Ncc/min, 1-8%O_2 / He balanced and 2%H_2O) half cycles. The *operando* UV−Vis spectra are reported as relative reflectance (R%) defined as: $R\%=R_{sample}/R_{reference}$, using Teflon® powder as reference. The UV-Vis spectra are analysed by using Multivariate Curve Resolution (MCR) to monitor the Cu^{II}/Cu^{I} redox dynamics and to quantify the relative amount of the two species.[3, 4]

Results and Discussion

Using *operando* UV-Vis Diffuse Reflectance (DR) spectroscopy coupled with a packed bed reactor, we validated the possibility to extrapolate relevant kinetic information from spectroscopic data. To the best of our knowledge, this approach represents a novelty for both kinetic and spectroscopic studies. Applying the developed experimental approach, we focused on monitoring *in operando* the redox dynamics and Cu sites speciation in Cu-CHA as a function of the reactive gas feed (e.g., in presence or absence of H_2O) and of the temperature (e.g., at 150°C or 200°C), during the RHC and the OHC.

Figure 1-a shows the DR UV-Vis spectra measured during the RHC transient (from grey to red curves). The initial and the final spectrum can be assigned to $[Cu_n(NH_3)_x(O,H)_y]^{II}$, with n ≤ 2 species (dashed grey curve), and to mobile $Cu^{I}(NH_3)_2$ moieties (red curve), respectively.[4] The $Cu^{II}\rightarrow Cu^{I}$ reduction is associated with the consumption of the Cu^{II} *d-d* feature in the visible range (broad signal centered at 14000 cm^{-1}) since Cu^{I} has a d^{10} close-shell configuration. In parallel, the $Cu^{II} \rightarrow Cu^{I}$ reduction is directly correlated with NO consumption monitored by gas phase analysis at the reactor outlet (Fig.1-b, red symbols). NO overall consumption monitored during RHC transients (16.0 µmol) confirms the 1:1 stoichiometry of the reduction between NO and Cu reduced,[1] and corresponds to an initial amount of Cu present as Cu^{II} of about 90%. Accordingly, the fraction of oxidized Cu^{II} sites independently quantified by the MCR analysis of UV-Vis spectra (90% at the beginning of the RHC transient, Figure 1-c, grey symbols). In addition, the observed dynamics were successfully simulated by an RHC kinetic model originally fitted to gas-phase only [1] (solid line in Fig.1-b and -c), assuming the Cu reduction rate to be 2nd order in Cu^{II} sites. The model nicely follows the dynamics of both Cu^{II} fraction and NO concentration, allowing for the estimation of a univocal apparent rate constant. These results provide clear evidence of the potential of the adopted approach in quantitatively describing redox catalysis. This can be applied to the study of metal-based catalysts, aiming at elucidating the active site structure–activity relation under kinetically relevant conditions.

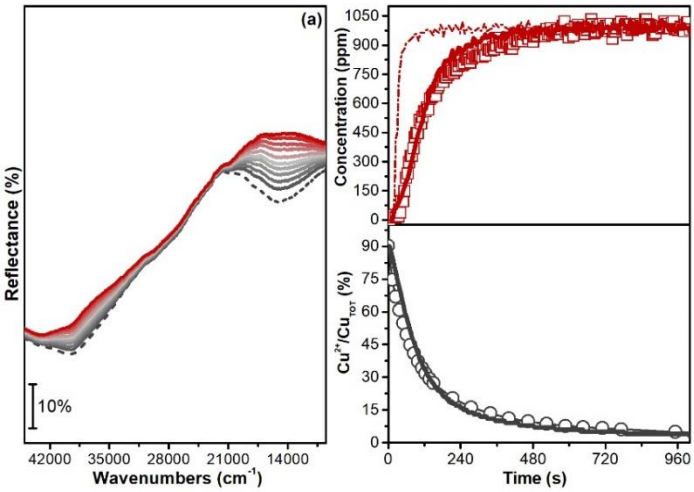


Figure 1(a) operando UV-Vis DR spectra during a RHC transient at 175°C; (b) CuII reduction dynamics from spectroscopic data (symbols) model predictions (solid line); (c) NO inlet (dashed line) gas phase NO (empty symbols) and model predictions (solid line)

References

1. F. Gramigni, N. D. Nasello,N. Usberti,U. Iacobone,T. Selleri,W. Hu, S.Liu, X. Gao, I. Nova, E. Tronconi, *ACS Catal*., **2021,** *11*, 4821–4831
2. C. Negri, T. Selleri, E. Borfecchia, A. Martini, K.A Lomachenko, T.V.W. Janssens, M. Cutini, S. Bordiga, G. Berlier, *J. Am. Chem. Soc.* **2020**, *142*, 15884–15896
3. C. Negri, R. Colombo, M. Bracconi, A. Donazzi, A. Lucotti, M. Tommasini, and M. Maestri, *Catal. Sci. Technol*., **2024**, *14*, 1318–1327
4. C. Negri, N. Usberti, G. Contaldo, M. Bracconi, I. Nova, M. Maestri, E. Tronconi, *Angew. Chem*., **2024**, *63*, e202408328

Spectroscopic investigation of In_2O_3-ZrO_2 catalyst for CO_2 hydrogenation to methanol

Marco Pietro MEZZAPESA*[,1], Fabio SALOMONE[1], Enrico SARTORETTI[1], Raffale PIRONE[1], Samir BENSAID[1]
[1]*Politecnico di Torino, Department of Applied Science and Technology (DISAT), Corso Duca degli Abruzzi 24, 10129 Turin, Italy.*
** marco.mezzapesa@polito.it*

Significance and Relevance

This study highlights the significance of CO_2 valorization via hydrogenation, focusing on an In_2O_3/m-ZrO_2 catalyst. This catalyst demonstrates superior methanol selectivity, supported by *in-situ* and *operando* spectroscopic analyses that revealed key reaction mechanisms, such as the role of In_2O_3 vacancies and m-ZrO_2 in facilitating CO_2 hydrogenation. These findings contribute to advancing catalytic technologies for sustainable methanol production, offering potential improvements in performance and selectivity over conventional systems.

Preferred and 2nd choice for the topic: Fundamental advances in understanding catalysis / CO_2 utilization and recycling
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Reducing greenhouse gas emissions is a pressing challenge that can be tackled by CO_2 valorization. Hydrogenation of CO_2 is a viable process route to obtain high-value-added products (e.g., methanol, olefins, kerosene, etc.). Methanol is a high-value product because of its many applications such as a solvent, fuel additive, and chemical building block, and it could be used for producing other high-added-value products such as olefins, gasoline, and so on. The CO_2 hydrogenation process occurs in a catalytic reactor at high pressure (50 – 100 bar) and in a temperature range of 200 – 300 °C. The commercial catalyst is Cu/ZnO/Al_2O_3 which has good CO_2 conversion but limited methanol selectivity[1]. Among the various alternative catalysts, In_2O_3/m-ZrO_2 (9 wt.% of In, m = monoclinic) is very interesting[2]. This catalyst promises good catalytic performance, mainly in terms of higher methanol selectivity compared to commercial materials. The aim of this work is a spectroscopic investigation (with *in-situ* and *operando* techniques) to deepen the knowledge of reaction mechanisms and interaction between catalyst and reactant/product substances.

Materials and Methods

The catalyst was synthesized using a gel oxalate precipitation-deposition method, where m-ZrO_2 was first obtained by precipitating $ZrO(NO_3)_2$, followed by calcination. In_2O_3 (10.9 wt.%) was then deposited on zirconia and calcined again. The powder was characterized using techniques like N_2 physisorption, H_2-TPR, CO_2-TPD, X-ray diffraction, and electron microscopy. FT-IR spectroscopy, in both *in-situ* and *operando* modes, was used to study the catalyst. *In-situ* analysis involved surface cleaning, activation, and CO_2 exposure as suggested by Tsoukalou[3]. Whereas, the *operando* analysis simulated reaction conditions (75% H_2 + 25% CO_2) at high pressure (7 bar) and temperature (200-300 °C). Furthermore, operando tests were performed with and without reductive pretreatment (200 °C, Ar or H_2/N_2).

Results and Discussion

The synthesis method successfully yielded the desired catalyst, as confirmed by XRD patterns in Figure 1(a), which indicate the presence of m-ZrO_2 and the expected fraction of In_2O_3. A comprehensive spectroscopic study, including *operando* and *in-situ* experiments, revealed significant interactions between CO_2, H_2, and the catalyst surface, suggesting a crucial role for In_2O_3 vacancies and m-ZrO_2 in the hydrogenation process. Specifically, FT-IR spectra in the 2700–3100 cm^{-1} region (Figure 1(b)) demonstrated the formation of formate (HCOO*) and methoxy (CH_3O*) species when the catalyst was exposed to an H_2/CO_2 mixture. These species are directly associated with methanol production, as

reported in the literature, and no peaks corresponding to CO or its production intermediates were detected, indicating high methanol selectivity[4,5]. This result aligns with previous studies, such as that of Martin et al[2], which estimated a methanol selectivity of 100%. *Operando* studies also explored catalyst activation, showing that intermediate species such as formates and methoxy groups only appeared after In_2O_3 was subjected to a reducing pretreatment. Additionally, the in-situ experiments (Figure 2) provided insights into H_2 splitting and CO_2 interaction mechanisms, suggesting that this catalyst may outperform others, particularly those featuring different ZrO_2 crystalline phases due to hydrogen carbonate formed over the activated catalyst. In conclusion, the combination of structural and spectroscopic analyses highlights the efficiency of the synthesized catalyst, particularly its high methanol selectivity and enhanced performance, which is likely due to the synergistic role of In_2O_3 vacancies and m-ZrO_2 in facilitating hydrogenation processes and promoting optimal CO_2 interaction.

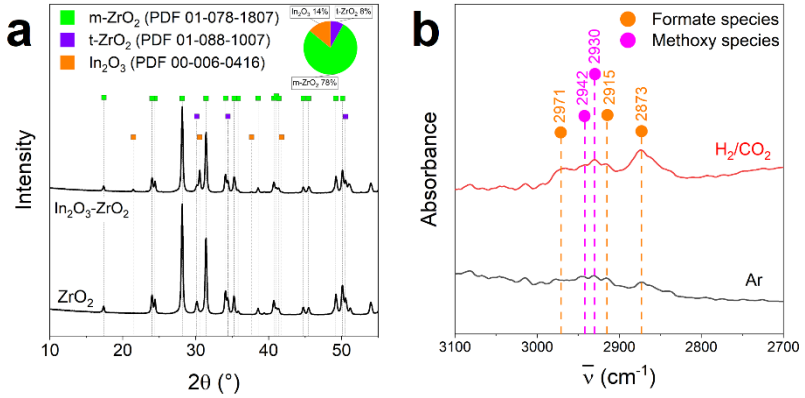


Figure 1. (a) XRD patterns for ZrO_2 and In_2O_3/m-ZrO_2 synthesized. The figure also shows the semi-quantitative analysis results for In_2O_3/m-ZrO_2. **(b)** *Operando* FT-IR spectra of In_2O_3/m-ZrO_2 captured in inert and reactive flow at 200 °C and 7 bar[4,5].

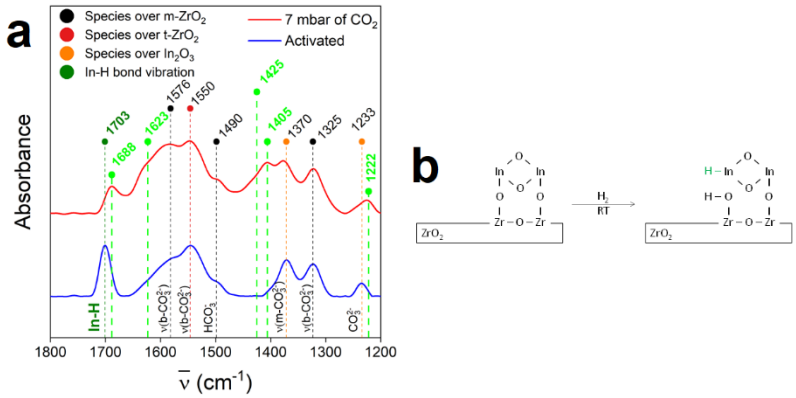


Figure 2. (a) FT-IR spectra of In_2O_3/m-ZrO_2 after H_2-dissociative adsorption with the method proposed by Tsoukalou[3]. **(b)** Hypothetic H_2-dissociative adsorption mechanism over In_2O_3/m-ZrO_2[3].

References

1. A. Álvarez, A. Bansode, A. Urakawa et al., Chem. Rev. **2017**, 117, 9804-9838
2. Martin et al., Angw. Chem. Int. Ed. **2016**, 55, 6261-6265
3. Tsoukalou et al., Catalysis Today **2022**, *387*, 38-46
4. Tsoukalou et al., J. Phys. Chem. C **2022**, 126, 1793-1799
5. Dang et al., Sci. Adv. **2020**, 6

Acknowledgments

Fabio Salomone and Enrico Sartoretti acknowledge the Italian Ministry of University and Research (MUR), program FSE REACT-EU PON Ricerca e Innovazione 2014-2020 (D.M. 1062/2021). Project funded under the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3 - Call for tender No. 1561 of 11.10.2022 of Ministero dell'Università e della Ricerca (MUR); funded by the European Union – NextGenerationEU. Project code PE0000021, Concession Decree No. 1561 of 11.10.2022 adopted by Ministero dell'Università e della Ricerca (MUR), CUP - to be indicated by each Beneficiary, according to attachment E of Decree No. 1561/2022, Project title "Network 4 Energy Sustainable Transition – NEST".

ME-PSD IR spectroscopy to study CO Oxidation reaction under Pt/Al_2O_3 catalyst

Nassar N.*, Djaafri A., Richard M., Dujardin C., Tougerti A., Cristol S.*
University of Lille, CNRS, Centrale Lille, ENSCL, University of Artois, UMR 8181-UCCS- Unité de Catalyse et Chimie du Solide, F-59000 Lille, France
** nabil.nassar@univ-lille.fr*

Significance and Relevance

Applying ME-PSD IR spectroscopy shine new insights of CO oxidation reaction mechanism occurring on Pt/Al_2O_3 catalyst. Based on these experiments, a new decomposition of the IR spectra of adsorbed CO is proposed.

Preferred choice for the topic: Fundamental advances in understanding catalyst
Preferred presentation: Oral preferred or Short Oral.

Introduction and Motivations

Dynamic behavior investigation of actives species involved in catalytic reaction is still highly challenging since a catalytic pathway is a combination of rapid adsorption and desorption of reactants/intermediates/products on ill-defined active surface sites.[1] Furthermore, the spectroscopic signal arising from non-active sites (spectators) is frequently stronger than that of actives sites, overwhelming key information on catalysis. One way to mitigate this problem is to apply Modulation Excitation Spectroscopy (MES)[2] which consists in a periodic perturbation of the state of the system by the variation of external parameter such as temperature, pressure, concentration... This rapid periodic perturbation of the system state will influence only the concentration profile of the active species which will oscillate at the frequency of the periodic excitation but with a phase delay. The concentration profile of species not responding to the periodic excitation (*i.e.* spectator species) will remain constant making possible their removal from the global signal by a post data acquisition mathematical treatment known as PSD (Phase Sensitive Detection). In this study we aim to monitor the dynamic behavior of actives species formed on the Pt/Al_2O_3 catalyst's surface during CO oxidation reaction by applying ME-PSD infrared (IR) spectroscopy (rapid looping from ^{12}CO to ^{13}CO while simultaneously recording time-resolved IR spectra). Indeed, although the Alumina-supported Pt catalyst (commonly used for CO and unburned hydrocarbon oxidation) has been extensively studied, the reaction mechanism of CO oxidation remains unclear and is still widely debated. Over 20 different steps have been proposed in the literature to explain this mechanism.[3]

Materials and Methods

Catalyst Synthesis. Pt/Al_2O_3 catalyst is prepared by incipient wetness impregnation of ɣ-Al_2O_3 support (specific surface area of 225 m^2g^{-1} and a pore volume of 0.76 cm^3g^{-1}) with platinum (II) acetylacetonate (Fluka) precursor salt to obtain 1 wt% metal loading. The sample was dried overnight at 85 °C, calcined 2 h under air flow at 500 °C (ramp 10 °C/min) and reduced with dihydrogen 2.5 h at 400 °C (ramp 5 °C/min).

ME-experiments. The catalyst is introduced in a home-made transmission IR reactor composed of 6 inlet and outlet channels (diameter 200 µm), in form of a square pellet (~10 mg and 1.21 cm^2) to perform *operando* experiments. The low dead volume of the reactor used here inferior to 0.5 cm^3, a required condition to obtain more relevant kinetic data for ME application. Spectra are obtained by using a ThermoScientific Nicolet 6700 FTIR spectrometer equipped with a MCT detector enable millisecond order spectra acquisition in rapid-scan mode. The cell is connected on one side to an automatic gas distribution system (Beckhoff®) composed of 4-way pneumatic valve upstream of the transmission IR reactor in order to switch the gas phase composition in isobaric and isotherm conditions. The ME PSD IR experiments are started once the system reach its steady state, only then the switching of the reactant from ^{12}CO to its labelled counterpart ^{13}CO is performed (sending 2000 ppm of $^{12}CO + O_2$ for 15s on the catalyst surface, then we switch to 2000 ppm of $^{12}CO + O_2$ also for 15s,

the gas flow rate was 12ml/min), under a constant temperature of 119°C. This $^{12}CO \rightarrow {}^{13}CO$ gas switch step was repeated 100 times.

Results and Discussion

"Figure 1 (top) shows IR spectra recorded during the ME-IR experiment (time domain), along with demodulated spectra obtained after PSD signal processing (Figure 1, bottom). In the 'CO adsorbed on Pt' region, the isotope peak exchange is visible in the time domain. However, in the 'carbonate and CO adsorbed on 2 Pt' regions, the isotope peaks become distinctly evident following PSD signal processing. Similar peaks between 1400 and 1900 cm^{-1} are observed for both fundamental and harmonic frequencies. However, in the CO adsorbed on Pt region, two additional peaks appear at 2043 and 2093 cm^{-1} in the harmonic frequency. This is clear evidence of the presence of two distinct kinetic processes. Indeed, since k3 reflects the behavior of species reacting at a higher frequency than the system's fundamental perturbation, we can conclude that carbonate species and CO bridging on two Pt atoms exhibit a slower exchange rate than CO adsorbed on a single Pt atom. Note also that the exchange between ^{12}CO and ^{13}CO is a simpler reaction when adsorbed in a bridging position between two platinum atoms, whereas it is much more complex when adsorbed on a single platinum atom (additional peaks at 2043 and 2093 cm^{-1} for harmonic frequency).

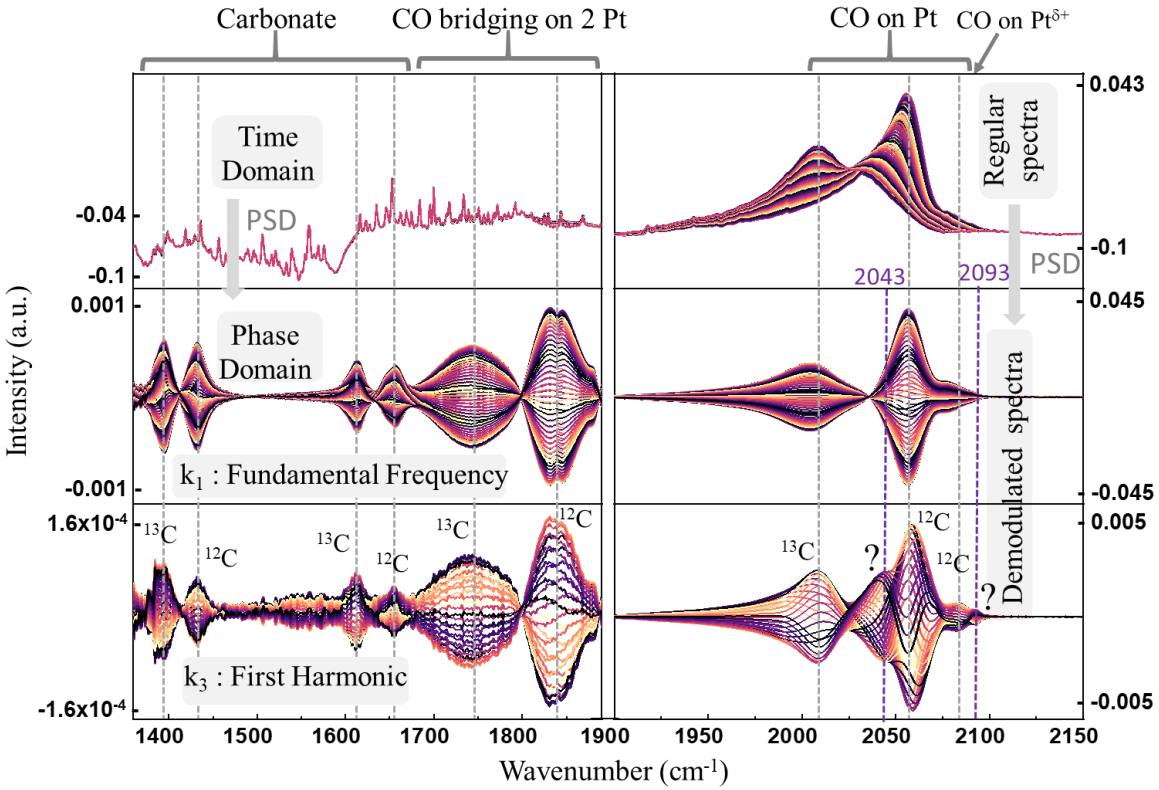


Figure 1. Upper. IR spectra recorded during $^{12}CO/^{13}CO$ looping experiment (time domain). Bottom. ME-IR spectra after PSD processing (demodulated spectra at k_1 and k_3)

References

1. D. S. Santilli and B. C. Gates, *Hydrocarbon Reaction Mechanisms*, Weinheim, Wiley-VCH., **2008**.
2. Müller P, Hermans I. *Applications of modulation excitation spectroscopy in heterogeneous catalysis*. Industrial & Engineering Chemistry Research, **2017**, 56(5): 1123
3. S. Salomons, R. E. Hayes, M. Votsmeier, A. Drochner, H. Vogel, S. Malmberg and J. Gieshoff, Appl. *Catal. B Environ*., **2007**, 70, 305–313

Acknowledgements

Thanks for the French National Research Agency who supported this work through the contract number ANR-21-CE50-0019 (MESCAT).

Low-Temperature redox kinetics for NH_3-SCR and N_2O formation over Cu-CHA catalysts

Nicola USBERTI[1], Andrea GJETJA[1], Isabella NOVA[1], Enrico TRONCONI[*,1],
Roberta VILLAMAINA[2], Maria Pia RUGGERI[2], Djamela BOUNECHADA[2], Andrew P. E. YORK[2], Jillian COLLIER[2]
[1]*Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, Via La Masa, 34, 20156 Milan, Italy*
[2]*Johnson Matthey Technology Centre, Blounts Court Road, Sonning Common, Reading RG4 9NH, UK*
*enrico.tronconi@polimi.it

Significance and Relevance

Results from this work highlight the significance of independently studying the two half-cycles of the low-T redox mechanism of NH_3-SCR over Cu-zeolite catalysts. This approach enables to identify the kinetics of Cu reduction, Cu oxidation, and side N_2O production, resulting in the accurate prediction of the low-T SCR activity of a model Cu-CHA catalyst across a wide range of representative conditions.

Preferred and 2nd choice for the topic:
Automotive and stationary emission control (or Fundamental advances in understanding catalysis)
Preferred presentation: *Oral preferred or Short Oral*

Introduction and Motivations

NH_3-SCR over copper-exchanged zeolite is the state-of-the-art process for NOx abatement from the exhaust gases of mobile sources. Recent literature works have been focused on the low-temperature (≤220 °C) Standard-SCR (STD-SCR) mechanism. It has been established that Cu active sites cycle between Cu^{II} to Cu^{I} in the Reduction Half-Cycle (RHC) and from Cu^{I} to Cu^{II} in the Oxidation Half-Cycle (OHC). Using Transient Response Methods (TRM), operando spectroscopy, Density functional Theory (DFT) and kinetic modelling, Tronconi and co-workers[1,2] and Daya et al.[3] proposed a dual-site mechanisms for both half-cycles, demonstrating that independent kinetic analysis of the RHC and of the OHC transients results in accurately simulating the NO conversion and the average oxidized Cu fraction at steady-state of STD-SCR. This work generalizes the proposed redox model, exploring the effects of temperature, Gas Hourly Space Velocity (GHSV), feed composition, pressure and washcoat loading on the Standard-SCR activity and on the undesired N_2O formation of a model honeycomb monolith Cu-CHA catalyst.

Materials and Methods

Experimental runs have been performed over monolith samples coated with a model Cu-CHA catalyst (1.67 % w/w Cu, SAR=25), placed in a stainless-steel tubular reactor, and tested at 150→200°C and GHSV≈40-120 kh^{-1}. The TRM protocol included: I) pre-oxidation with O_2 (8%) and NH_3 (500 ppm); II) reduction of the fully oxidized catalyst with NO (300-600 ppm) and NH_3 (500 ppm); III) STD-SCR, adding O_2 (1-12%) to NO and NH_3, IV) a second reduction step, shutting-off O_2 after STD-SCR steady-state, allowing the evaluation of the bed-average Cu^{II} fraction at STD-SCR steady-state ($\sigma =$ /). All tests were carried out in 2.3% H_2O using N_2 as diluent. Data were fitted by the PFR transient integral reactor model proposed by Nasello et al.[1] assuming: a) the RHC rate to be 1st and 2nd order in the NO concentration and the Cu^{II} fraction (= ( )σ^2); b) the OHC rate to be 1st order in O_2 and 2nd order in reduced Cu fraction (= ($_2$) $(1-\sigma)^2$). N_2O production kinetics at low temperature was added as an unselective Cu reduction step with rate 1st order in NO and with undefined nth order in the oxidized Cu fraction ($_2$ = $_2$ ( )σ). Finally, NO conversions, bed-average oxidized Cu fractions, and N_2O productions at STD-SCR steady-state were used as experimental responses in a multi-response non-linear least-squares regression to estimate the rate parameters that best fit the collected data.

Results and Discussion

TRM tests performed between 150 and 200°C allowed to collect NO conversions, oxidized Cu fractions and N_2O outlet concentrations at STD-SCR steady-state under different operating conditions. The activity shown by the catalyst is the result of the kinetic equilibrium reached between reduction and oxidation reaction rates (=). Combining the two rate expressions while neglecting the influence of the N_2O production on the overall NO conversion (only few ppm of N_2O produced), we derived the rate expression of the low-T Standard SCR shown in Eq.1. N_2O was confirmed to be the product of a side RHC reaction, following an apparent 3rd order dependence on the oxidized Cu fraction and a 1st order dependence in NO (steady-state rate expression shown by Eq.2). These assumptions allow both to nicely match the N_2O formation dynamics during the reduction step and to predict the steady-state N_2O make during the STD-SCR phase.

Collected steady-state data are used as experimental responses of a global regression, for a total of 48 kinetic runs. By minimizing the sum of the squared errors between experimental and simulated data, we obtain a single set of kinetic parameter estimates for the RHC, RHC_N_2O and OHC rate expressions (6 adaptive parameters, , and ,). Fit results are shown as parity plots in Figure 1, comparing experimental data and model simulations with the fitted kinetics for NO conversion (panel A, covering a wide range between 20% and 90%), average oxidized Cu fraction σ (panel B), and N_2O production (panel C) at STD-SCR steady-state. These results highlight the adequacy of the proposed low-temperature redox model in accurately predicting the Standard SCR over a wide range of conditions, with minimal and randomly distributed errors (average of ~3-5% on the NO conversion and average Cu fraction and of 0.25 ppm on the N_2O production). The model accurately describes the effects of temperature (150→200°C), NO (300→600 ppm) and O_2 (1→12%) concentrations, space velocity (40→120 kh^{-1}), and pressure (1→3 bara). Furthermore, the model was able to predict the results obtained over a monolith with increased washcoat loading. Notably, the kinetics from the global regression allow not only to effectively simulate the STD-SCR steady-state, but also the dynamics observed during the transient redox tests over the whole range of investigated operating conditions.

$$\text{STDSCR} = \frac{(\quad)\quad(\quad_2)}{(\sqrt{\quad(\quad)}+\sqrt{\quad(\quad_2)})^2} \quad \text{Eq.1} \qquad {}_2 = {}_2(\quad)\left(\frac{\sqrt{\quad(\quad_2)}}{\sqrt{\quad(\quad)}+\sqrt{\quad(\quad_2)}}\right)^3 \quad \text{Eq.2}$$

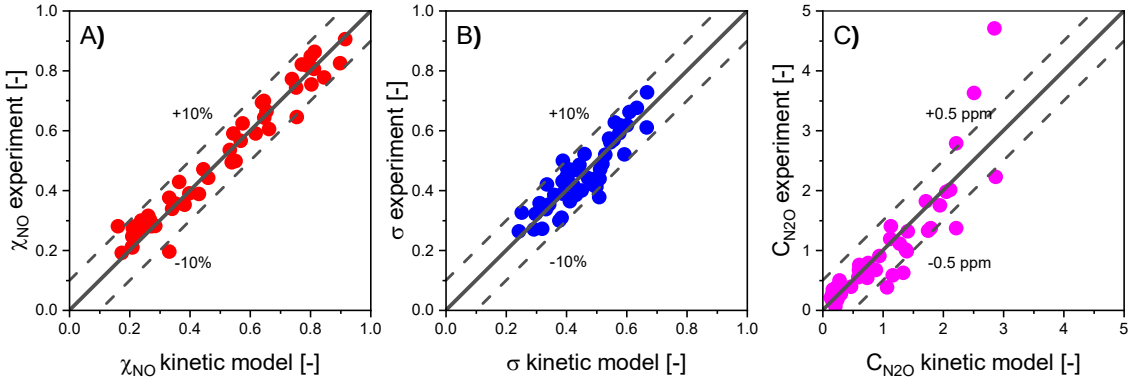


Figure 1. Experimental and simulated STD-SCR NO conversions (A), average oxidized Cu fractions (B) and N_2O (C) varying T (150→200 °C), GHSV (40→120 kh^{-1}), NO (300→600 ppm), O_2 (1→12 %) concentrations, and pressure (1→3 bara).

References

1. N. D. Nasello, N. Usberti, U. Iacobone, F. Gramigni, W. Hu, S. Liu, I. Nova, X. Gao, E. Tronconi, *ACS Catalysis* **2023**, *13, 4*, 2723−273.
2. C. Negri, N. Usberti, G. Contaldo, M. Bracconi, I. Nova, M. Maestri, E. Tronconi, *Angewandte Chemie International Edition* **2024**, *63, 41*, e202408328.
3. R. Daya, D. Trandal, U. Menon, D. J. Deka, W. P. Partridge, S. Joshi, *ACS Catalysis* **2022**, *12, 11*, 6418–6433.

Unlocking NOx Reduction Pathways in CO-Assisted NO Reduction over Ultra-Low Metal Content Catalysts Supported on Ceria-Zirconia

J.C MARTÍNEZ-MUNUERA[1], R. MATARRESE[2], L. CASTOLDI[2], L. LIETTI[2], A. GARCÍA-GARCÍA*[,1]
[1]*Grupo MCMA, Departamento de Química Inorgánica e Instituto Universitario de Materiales, Universidad de Alicante, Carretera de San Vicente del Raspeig s/n, 03690 San Vicente del Raspeig, Spain.*
[2]*Gruppo di Catalisi e Processi Catalitici, Dipartimento di Energia, Politecnico di Milano, Via La Masa 34, 20156 Milano, Italy.*
** a.garcia@ua.es*

Significance and Relevance

In order to gain detailed information on the mechanistic aspects involved in the CO-assisted NO reduction with the final purpose of avoiding the utilization of PGMs (Platinum Group Metals), which are featured by very high prices and very fluctuating, a fundamental study has been carried out with ultra-low metal contents as active phases (Cu, Ag and Co, as well as Pt taken as benchmark), supported onto ceria-zirconia, by combining the evaluation of the catalytic activity carried out by micro-reactor studies and the surface characterization in the course of the reaction by *operando* FT-IR analysis. Some pathways involved in the N-formation products were clarified related to the impact of the nature of the active phase used.

Automotive and stationary emission control and Fundamental advances in understanding catalysis. Short Oral.

Introduction and Motivations

Modern three-way catalysts (TWCs) for aftertreatment systems are remarkably effective for removing nitrogen oxides (NOx), carbon monoxide (CO) and hydrocarbons (HC) from gasoline vehicles. However, the most efficient last-generation gasoline combustion engines, that can significantly increase fuel efficiency, and hence, producing lower exhaust temperatures resulting from these power gains, are being revealed as a significant challenge towards current emissions control catalysts. On the other hand, commercial TWCs have been traditionally developed with formulations composed of platinum group metals (PGMs) supported on durable inorganic oxides. PGMs, as well known, are very active components towards the pollutants removal but featured by a very high and fluctuating cost[1]. In this context, the need of developing more inexpensive and efficient catalysts which can operate at the required lower temperatures is essential. In this work, several ceria-zirconia based catalysts with ultra-low metal contents have been prepared, characterised and tested for the model reaction (CO-assisted NO reduction), in the presence and the absence of O_2, in order to understand in a comprehensive way all the possible routes that are taking place during this reaction by quantifying all the reaction products, thus evaluating the corresponding N- and O-mass balances. *Operando* FT-IR experiments were also conducted providing a complementary overview of the involved processes under selected cases. All the pathways to form the N-reduction products are explored and tried to be explained on the basis of the catalysts' formulations. These whole findings may provide a basis for designing more active and selective catalysts.

Materials and Methods

$Ce_{0.8}Zr_{0.2}O_2$ support was synthesised by means of the conventional coprecipitation method in alkaline media. The catalysts were prepared by IWI of the support with the corresponding metal precursors' solutions, loading different percentages in weight with the aim to reach the same molar composition in metals (for Cu 0.20 wt.%, for Co 0.19 wt.%, for Ag 0.34 wt.%, and for Pt 0.61 wt.%, respectively). The solids obtained were calcined for 1 h at 500°C. The catalysts synthesised were characterized in terms of textural and structural properties (N_2 adsorption at -196°C, XRD, XPS, H_2-TPR and Raman spectroscopy). The oxygen storage capacity (OSC) was also evaluated at 150°C for all the samples by a TG-MS equipment[2]. Catalytic activity was performed in a wide temperature range (TPR

from 40°C up to 500°C) by using 86 mg of the sample mixed with 86 mg of quartz. For all the catalytic tests, the gas flow was fixed at 170 ml/min (GHSV of 90000 h^{-1}). All the catalysts were pre-treated using 5% O_2/He for 20 min at 500°C. Catalytic activity was analysed under: 1000 ppm CO/He; 1000 ppm NO/1000 ppm CO/He; 200 ppm NO/400 ppm O_2/1000 ppm CO/He. The same experimental procedure and protocol adopted for micro-reactor experiments was used in the *operando* FT-IR reactor cell.

Results and Discussion

Figure 1 depicts the corresponding product profiles of the CO-assisted NO reduction, as a function of temperature, for two representative catalysts (Pt0.6CZ and Cu0.2CZ). Both catalysts present a notable activity towards CO oxidation/NO reduction but with remarkable differences. The curves exhibit complex profiles, (especially for the case of Cu-catalyst), suggesting the possible co-existence of several reaction routes and their intrinsic complexity. By a detailed inspection of the corresponding mass balances versus temperature (not shown), the CO_2 emission profiles and the N-products emission profiles, estimated from the contribution of N_2, (main N-product), N_2O and NH_3, (suggested to be a secondary product due to the reaction of H_2, whose presence can be accounted for the well-known WGS reaction, with NO) are almost completely overlapped. This indicates a "coupled" process of CO oxidation/NO reduction, where CO_2 and N_2 (86% of selectivity) are the main reaction products. Conversely, the whole routes taking place during the CO-assisted NO reduction are much more complicated for Cu0.2CZ. At low temperatures, some events related to the fast reduction of generated surface nitrites by CO seem to occur (confirmed by *operando* studies). After this, the catalytic performance might proceed in sequential steps where CO molecules attack to the catalyst's surface, producing CO_2 and oxygen vacancies (this is consistent with CO-TPR profiles for this catalyst). Subsequently, NO molecules interact with the oxygen vacancies (by electronic transfer processes), thus generating N_2O as first product, and, subsequently, N_2. This sequential product generation is congruent with the proposed mechanism and far from that of Pt (whose onset temperatures for N_2O and N_2 are coincident), and relevant populations of $Pt^{\delta+}$-carbonyls and isocyanate species were identified as main intermediate. O-emission balance, but interestingly N-balance are fulfilled (N_2 selectivity 68%). However, the NO reduction is not coupled with the CO conversion, since CO oxidation proceeds first and, subsequently, the NO reduction, which seems to be conditioned by the oxygen vacancy population ("freshly created"), which is highly promoted by copper supported on CZ.

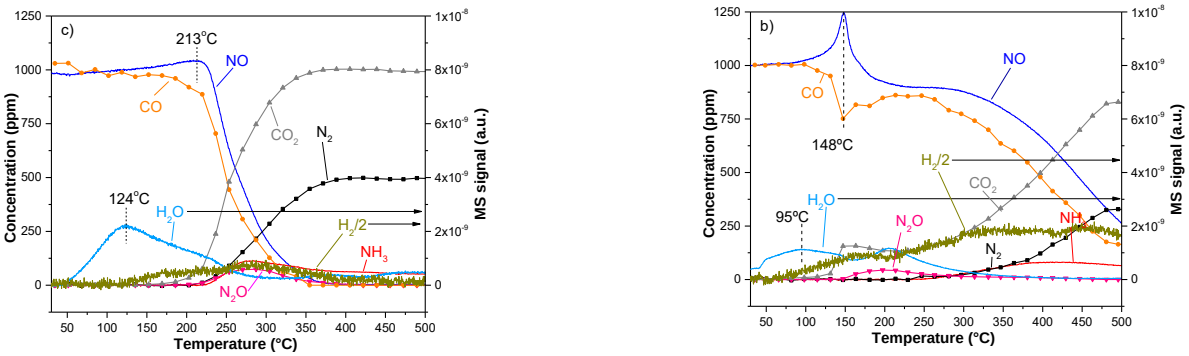


Figure 1. Evolution of reactants and products during the CO+NO reaction: a) Pt0.6CZ and b) Cu0.2CZ.

References

1. J.C. Martínez-Munuera et al, *Journal of Rare Earths* **2024**, 42, 1669.
2. J.C. Martínez-Munuera et al, *Applied Surface Science* **2020**, 529, 147019.

Acknowledgements

Financial support from Generalitat Valenciana (CIPROM/2021/070) is gratefully acknowledged.

Sustainable energy storage materials from waste hazelnut shell biomass

Stefania VOLANTE*[1], Domenico LICURSI[1], Federico Maria VIVALDI[1], Pietro ZACCAGNINI[2], Federico BELLA[2], Fabio DI FRANCESCO[1], Claudia ANTONETTI[1]

[1]*University of Pisa, Department of Chemistry and Industrial Chemistry, Via G. Moruzzi 13, Pisa, Italy*

[2] *Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129, Torino, Italy*

** stefania.volante@phd.unipi.it*

Significance and Relevance

In this work, different activated carbons (ACs) were synthesized starting from hazelnut shell (HS) and employed to manufacture supercapacitor (SC) electrodes. Moreover, copper oxide post-doping was explored to further enhance the pristine ACs performances. Preliminary electrochemical tests identified two ACs (HTC-AC and PYRO-AC) and one doped-AC (CuO-HTC-AC) as the most promising ones, which were further investigated by optimizing the electrode preparation procedure. Two of the tested samples displayed a specific capacitance value of about 500 F/g, significantly outperforming commercial carbons.

Preferred and 2nd choice for the topic: 1. Sustainable and clean energy production and transport; 2. Green chemistry and biomass transformation, renewable resources conversion
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The urgent need to move away from fossil fuels has increased interest towards the development of alternative energy sources and storage solutions. [1] In this context, SCs are attracting much interest due to their high-power density, long life and fast charging capability. According to the charge storage mechanisms, SCs can be classified into electric double layer capacitors (EDLCs), pseudocapacitors and hybrid supercapacitors (HSCs), these latter combining both charge storage mechanisms.[1] EDLCs store energy by accumulating charges on the surface electrode, typically consisting of carbon materials, such as nanotubes, graphene and ACs. In this context, biomass-derived carbons offer a sustainable alternative for the production of EDLC electrodes. Conversely, pseudocapacitors achieve higher capacitance than EDLCs as they store energy through rapid and reversible redox reactions occurring on the electrode surface. In this case, metal oxides and conductive polymers are the most employed materials. In particular, CuO stands out for its high theoretical pseudo-capacitance, good conductivity, environmental friendliness and straightforward preparation. [2] On this basis, the combination of porous carbon materials with pseudocapacitive compounds, such as CuO, represents a promising strategy for developing new, efficient and sustainable composite electrodes for energy storage solutions. In this work, the HS waste biomass was employed as the precursor for the synthesis of three ACs and a char.[3] Moreover, the two most promising ACs were doped with CuO. The physicochemical and electrochemical properties of the synthetized HS-derived carbons were characterized to evaluate their potential for electrode fabrication in supercapacitors. This study investigates the influence of thermal treatments on the electrochemical performances of char, at the same time, proposing an eco-friendly approach for biomass repurposing with potential economic benefits within a circular economy framework.

Materials and Methods

The three ACs were obtained through chemical activation pyrolysis employing KOH as the activating agent, with the precursor/KOH weight ratio of 1/4 at 600°C per 1 h under N_2 atmosphere, according to our previously optimized procedure. [3] The first AC was directly synthesized from the raw biomass (HS-AC), the second one from the hydrochar derived from the hydrothermal carbonization (HTC) of HS (HTC-AC), performing the HTC step at 220°C for 5 hours with the biomass loading of 20 wt%. [4] The third AC sample (PYRO-AC) was obtained by a three-step procedure including 1) HTC followed by 2) pyrolysis in the absence of KOH (600°C for 1 h under N_2 atmosphere) and 3) KOH activation pyrolysis. Lastly, the char obtained after pyrolysis post-treatment of the hydrochar (HTC-PYRO) was also tested for

comparison.[3] CuO-doping of the most promising ACs was performed modifying a procedure already available in the literature,[2] by treating the selected AC with copper(II) acetate solution at pH 10, to precipitate copper(II) hydroxide. The products were recovered by centrifugation and heat-treated at 150 °C to favor the CuO deposition, yielding CuO-HTC-AC and CuO-PYRO-AC. Electrochemical measurements were carried out using two three-electrode setups. The first employed Ag/AgCl and Pt wires as reference and counter electrodes, with KNO_3 or KOH as electrolytes, and a nickel foam-based working electrode prepared by depositing a slurry of active material 80 wt%, carbon black 10 wt% and polyvinylidene fluoride 10 wt%. The second configuration employed a Swagelok cell with lithium metal as reference and counter electrode, LP30 as the electrolyte, and a Doctor Blade-prepared working electrode with a slurry containing active material 85 wt%, carbon black 10 wt%, (carboxy methylcellulose + styrene butadiene rubber at 1:2 weight ratio) 5 wt%. Cyclic voltammetry (CV) and charge/discharge tests assessed the materials' electrochemical performance.

Results and Discussion

Among the bare samples, HTC-AC and PYRO-AC exhibit pseudo-rectangular shape CV curves in both cathodic and anodic zones (Figure 1) in KNO_3, indicating good capacitive performance attributed to their superior surface properties and high specific surface area (SSA). In fact, HTC-AC and PYRO-AC showed higher SSA values (1000 m^2/g and 1421 m^2/g, respectively) than the other two tested materials ($SSA_{HS\text{-}AC}$= 815 m^2/g; $SSA_{HTC\text{-}PYRO}$= 388 m^2/g), highlighting that the pretreatment and activation of the raw biomass are necessary steps to achieve good surface properties. The corresponding CuO-doped ACs were prepared and tested. A significant improvement in the anodic region was observed for the CuO-HTC-HAC, which doubled the specific capacitance value compared to its undoped precursor due to an improved electrical conductivity and charge storage capacity. The most promising ACs (HTC-AC, CuO-HTC-AC and PYRO-AC) were further investigated to explore the electrochemical behavior of these materials and assess possible effects of the manufacturing method of the working electrode on the electrochemical performances. We focused on the cathodic region, using also the Swagelok type cell, and achieved capacitance values (HTC-AC ≅ 250 F/g, PYRO-AC ≅ 500 F/g, CuO-HTC-AC ≅ 500 F/g) much higher than those claimed for commercial carbons (100-200 F/g). [5]

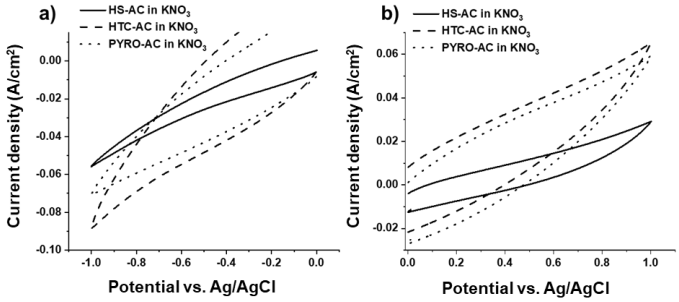


Figure 1 Cyclic voltammograms of HS-AC, HTC-AC and PYRO-AC in KNO_3 (2.5 M) in a potential window between a) -1 to 0 V (cathodic zone) and b) 0 to 1 V (anodic zone) at the scan rate of 0.1 Vs^{-1} per 1 cycle.

References

1. J. Sun, B. Luo, H. Li, *Adv. Energy Sustainability Res.* **2022**, *3*, 2100191.
2. Y. Zhan, J. Bai, F. Guo, H. Zhou, R. Shu, Y. Yu, L. Qian, *J. Alloys Compd*. **2021**, *885*, 161014.
3. D. Licursi, C. Antonetti, N. Di Fidio, S. Fulignati, P. Benito, M. Puccini, S. Vitolo, A.M. Raspolli Galletti, *Waste Manag.* **2023**, *168*, 235-245.
4. D. Licursi, C. Antonetti, S. Fulignati, S. Vitolo, M. Puccini, E. Ribechini, L. Bernazzani, A.M. Raspolli Galletti, *Bioresour. Technol*. **2017**, *244*, 880-888.
5. A.G. Olabi, Q. Abbas, M.A. Abdelkareem, A.H. Alami, M. Mirzaeian, E.T. Sayed, *Batteries* **2023***, 9*, 19.

Acknowledgements

The authors are grateful to the European Union and Italian “Ministero dell’Istruzione, dell’Università e della Ricerca” for the financial support provided through the PNRR project Sustainable Mobility Center CNMS, Spoke 13 Electric Traction Systems and Batteries (ETSB), CUP I53C22000720001.

Improving oil quality from waste plastics pyrolysis: aromatization and dehalogenation activity using MFI zeolites

Jennifer CUETO*[,1], Alberto PINTO[1,2], Lidia AMODIO[1,2], Pavla ELIÁŠOVÁ[3], Patricia PIZARRO[1,2], Kenta IYOKI[4], Tatsuya OKUBO[4], Tareq W.M. Amen[5], Nao Tsunoji[5], Jiří ČEJKA[3], David P. SERRANO[1,2]

[1]*Thermochemical Processes Unit, IMDEA Energy, Avda. Ramón de la Sagra 3, 28935, Móstoles, Madrid, Spain*

[2]*Chemical and Environmental Engineering Group, Rey Juan Carlos University, Móstoles, Madrid, Spain*

[3]*Dep. of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Prague, Czech Republic*

[4]*Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Tokyo, 113-8656, Japan*

[5]*Department of Applied Chemistry, Graduate School of Advanced Science and Engineering, Hiroshima University, 1-4-1 Kagamiyama, Hiroshima, 739-8527, Japan*

** jennifer.cueto@imdea.org*

Introduction and Motivations

The shift to a circular economy has heightened the focus on energy and carbon efficiency, making plastics recycling essential due to their energy-intensive production, widespread use, and environmental persistence. Chemical recycling, especially pyrolysis, is gaining attention for converting plastic waste into petrochemical feedstocks like olefins and aromatics. In this way, pyrolysis thermally decomposes plastics into valuable products but faces challenges from feedstock contamination and quality issues. In particular, the presence of halogenated species (mostly Cl-containing compounds) strongly limits the possible upgrading of the waste plastics pyrolysis oil in refinery units. Zeolites, particularly ZSM-5 (MFI), have emerged as highly effective catalysts in post-pyrolysis treatments to address these issues. ZSM-5 is known for its unique microporous structure and acidity, which enhance oil quality by increasing light hydrocarbon yields, reducing impurities such as halogens, and optimizing the hydrocarbon composition.[1] In this context, this study aims to improve the quality of an oil obtained from the pyrolysis of real waste plastics by exploring how the synthesis method and the properties of ZSM-5 zeolite affect the efficiency of the dehalogenation process and the generation of aromatic compounds in the treated oil.

Materials and Methods

The feedstock oil was characterized using various analytical techniques[1]. This oil exhibits a notably high chlorine concentration (290 ppm) and is predominantly enriched with aliphatic compounds, particularly paraffins, whereas the content of aromatic hydrocarbons is small (c.a. 5.5 wt%). Additionally, it contains a significant fraction of heavy compounds, comprising 43.5 wt%, which are undetectable by GC-MS. A ¾" diameter fixed-bed reactor was used for the oil upgrading catalytic tests, with the oil being fed through an HPLC pump. Four ZSM-5 zeolite samples were tested at 450 °C and a WHSV of 5 h^{-1}. These included one microcrystalline and three nanocrystalline zeolites, each synthesized using distinct methods (Table 1): *nano 1* by milling the microcrystalline zeolite, *nano 2* from an amorphous aluminosilicate hydrogel made with fumed SiO_2 and sodium aluminate, using buthylmethylpyrrolidinium hydroxide (BMC5) as the organic structure-directing agent (OSDA), and *nano 3* through hydrothermal conversion of FAU, also employing BMC5 as OSDA[2]. At the reactor outlet, a condensation system allowed liquid samples to be taken at different reaction times, which were analyzed using the same techniques as the feedstock oil. The gases were collected with the help of a totalizer, and their composition was determined using μ-GC.

Table 1. Characterization of the feedstock oil and zeolite samples. [1]: CHNS-O, [2]: AOD-IC, [3]: GC-MS, [4]:ICP-MC, [5]: N_2 adsorption (77 K).

Oil elemental composition (wt%)		Raw oil molecular composition (wt%)[3]		Zeolite characterization					
				Sample	Si/Al[4]	S_{BET} (m^2/g)[5]	S_{Ext} (m^2/g)[5]	V_{mic} (cm^3/g)[5]	V_{total} (cm^3/g)[5]
C[1]	85.52	Mono-aromatics (MAH)	5.5	ZSM-5 (micro)	13.9	431	36	0.16	0.22
		Naphthenes (NAPH)	7.2	ZSM-5 (nano 1)	14.0	415	87	0.14	0.33
H[1]	14.45	Olefins (OL)	8.2	ZSM-5 (nano 2)	38.6	363	115	0.15	0.16
Cl[2]	0.029	Paraffins (PAR)	35.6	ZSM-5 (nano 3)	39.4	385	170	0.16	0.16

Results and Discussion

Figure 1 summarizes the key results of oil upgrading experiments conducted with various zeolites. The data indicate that zeolites synthesized using BMC5 as OSDA (nano 2 and nano 3) exhibit no significant differences in performance. However, a notable distinction arises when comparing ZSM-5 (micro) with its milled counterpart (ZSM-5 nano 1). Milling the ZSM-5 zeolite substantially reduces gas yield from 15.7 wt% to 6.7 wt%, reflecting a diminished cracking capacity. This reduction can be attributed to a decrease in Brønsted acidity caused by the milling process (0.9 and 0.52 mmol/g for micro and nano1, respectively).

All tested zeolites demonstrated significant activity in aromatization reactions, particularly noteworthy given the initial aromatics content of 5.5 wt% in the feed oil. The differences in performance were relatively modest in spite of the great variations observed between the zeolite properties. It can be envisaged that the lower Al content of samples ZSM-5 (nano 2) and ZSM-5 (nano 3) is compensated by their enhanced accessibility due to their larger surface area. Thus, the highest yield of aromatics, 15.1 wt%, was achieved with ZSM-5 (nano 2).

Another noteworthy parameter is the chlorine concentration in the upgraded oil and how it evolves as a function of time on stream (Figure 1c). Also, in this case, zeolites ZSM-5 (nano 2) and ZSM-5 (nano 3) exhibit greater dehalogenation efficiency and a better stability showing lower deactivation along the time on stream. Among these, ZSM-5 (nano 3) achieves the lowest chlorine concentration (40 ppm at 0.5 h). Conversely, ZSM-5 (micro) and ZSM-5 (nano 1) zeolites demonstrate a lower dehalogenation capacity, with a fast increase in the oil Cl content along the time on stream. Therefore, regarding the oil dehalogenation process, the zeolite accessibility also plays a more relevant role than the Al content.

Based on these findings, it can be concluded that ZSM-5 zeolites are highly promising materials for improving the quality of waste plastics pyrolysis oil, making them suitable candidates for the development of pre-treatment processes before injecting the upgraded oils into existing refinery units.

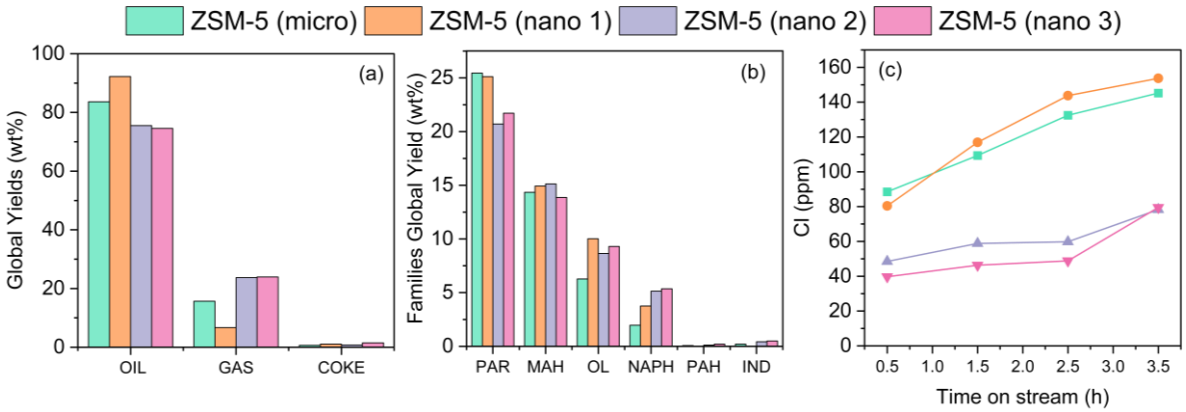


Figure 1. (a) Global mass yields of the different fractions, (b) global yield of the main families obtained in the oil, (c) Cl concentration in the oil as a function of the reaction time on stream.

References

[1] J. Cueto, G. Pérez-Martin, L. Amodio, M. Paniagua, G. Morales, J. A. Melero, D. P. Serrano, Chemosphere **2023**, *339*, 139784.

[2] T. Tanigawa, N. Tsunoji, M. Sadakane, T. Sano, Microporous and Mesoporous Materials **2019**, *277*, 115-123.

Acknowledgements

This work is part of the action PCI2023-143433, funded by MCIN/AEI/10.13039/501100011033 and by the European Union. The authors also acknowledge the EIG Concert Japan program (Nr. 8123003).

Kinetic Investigation of Ammonia Decomposition over Ru/CeO_2 Catalysts Synthesized by Conventional IWI and Novel Mechanochemical Approaches

Yi QIU[1], Ivan CONTI[1], Nicole BENDAZZOLI[1], Rudy CALLIGARO[2], Alessandro TROVARELLI[2], Elisabetta IENGO[3], Enzo ALESSIO[3], and Alessandra BERETTA*[1]

[1] *Dipartimento di Energia, Politecnico di Milano, Via Lambruschini 4, 20156, Milano, Italy*

[2] *Dipartimento Politecnico di Ingegneria e Architettura, Università degli Studi di Udine, via del Cotonificio 108 33100, Udine, Italy*

[3] *Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste, Via L. Giorgieri 1, 34127, Trieste, Italy*

**alessandra.beretta@polimi.it*

Significance and Relevance

Ru is unanimously recognized as catalyst of choice for NH_3 decomposition, but the rate of reaction is strongly limited by the Ru–H* interaction, especially at higher temperatures (required for complete NH_3 conversion). The role of the support is of key importance. CeO_2 offers outstanding performance and minimizes H* poisoning, and both factors are emphasized over the catalyst obtained by milling.

Preferred and 2nd choice for the topic: ***Preferred: H_2 storage and transportation, green H_2 production, hydrogen vectors; 2nd choice: Sustainable and clean energy production and transport***
Preferred presentation: **Oral preferred or Short Oral**

Introduction and Motivations

Green NH_3 is considered as a promising H_2 carrier because of its high hydrogen density, well-developed technologies and infrastructures for synthesis, storage and transportation[1]. Catalysts for NH_3 decomposition are actively studied in the literature, which documents the superiority of Ru[2]. Among supports, CeO_2 is attracting attention as an electron donor which could facilitate N–H bond cleavage and associative desorption of N* and H* species[3]. In this work, Ru/CeO_2 catalysts were prepared by conventional impregnation and novel mechanochemical methodology to investigate the role of the support on the activity and kinetics of NH_3 decomposition. The performance was evaluated by comparison with a reference Ru/Al_2O_3 catalyst.

Materials and Methods

Ru/Al_2O_3-IWI and Ru/CeO_2-IWI catalysts were prepared via incipient wetness impregnation, using $Ru(NO)(NO_3)_3$ as Ru precursor. Ru/CeO_2-BM was obtained by ball milling a mixture of $Ru_3(CO)_{12}$ (thus starting from Ru with metal character) and CeO_2 at 15 Hz in a zirconia jar with a single zirconia ball for a total of 20 min. Catalysts were characterized by XRD, Raman, DRIFTS, CO chemisorption and HR-TEM. Prior to tests, the catalyst was reduced in flowing H_2 at 450 °C. NH_3 cracking was tested in micro-fixed bed unit, with diluted feeds (0.3–2.5% NH_3 in He). H_2 cofeeding tests were performed up to 25%, to characterize the kinetics under fully representative conditions. The effect of N_2 was also studied by cofeeding 10% N_2 with NH_3. All the experiments were performed at 20,000 Nl/h/kg_{cat}. The modelling analysis was based on 1D pseudo-homogeneous isothermal and isobaric reactor model.

Results and Discussion

The bulk of characterization results suggests a very high dispersion of Ru for all the catalysts. In the CeO_2-catalysts obtained by both IWI and BM, Raman and DRIFTS showed intense signals associated with interfacial Ru–O–Ce sites, supporting the hypothesis of strong metal support interaction facilitated by high dispersion.

Tests were performed to highlight the main kinetic dependences and evaluate the effect of the nature of the support and of the preparation procedure. Figure 1 shows a comparison of the measured NH_3 conversion at the reference condition of 1% NH_3 in He; it is clear that the Ru/CeO_2 catalysts outperformed the reference Ru/Al_2O_3 catalyst. Assuming pseudo-first order kinetics (Arrhenius plots, Figure 2), a slope change is observed for both Ru/CeO_2 catalysts, which suggests a change of the rate

determining from below and above 300°C. Extensive kinetic investigations were performed over all catalysts, consisting of data at varying NH_3 concentration, H_2-cofeed and N_2-cofeed and crossed effects. Trends were rationalized by a kinetic modelling. In the case of Ru/Al_2O_3 the kinetic dependences are consistent with the assumption that the rate determining step is the second N–H cleavage and that H* is the most abundant surface intermediate, which results in a first order dependence on NH_3 and a negative order -1.5 on H_2. The solid lines in Figure 3 show the model fit according to such conclusions.

Instead, in the case of both Ru/CeO_2 catalysts, the low temperature data are best described by assuming that N* associative desorption is rate determining and N* is accordingly the most abundant surface intermediate, while at higher temperature the observed trends suggest that NH_3 activation (first N–H cleavage) and H* poisoning are the controlling factors. The solid lines in Figure 4 show the very satisfactory description obtained by developing a model that interpolates the two limiting kinetic models and describes a change of the reaction order on NH_3 from zero to 1.

H_2 and NH_3 adsorption/desorption experiments are being performed to investigate the nature, the abundance and adsorption strength of surface intermediates on Ru sites, and the effect of supports; these studies are of fundamental importance to support the mechanistic hypotheses. Dynamic experiments, for instance, show high retention of hydrogen over CeO_2, which suggests that Ru–H* bond is weakened by the H*–support interaction, thus promoting the reaction kinetics.

The ball milled Ru/CeO_2 obtained from the organometallic precursor showed higher activity and further reduced H* poisoning, possibly the result of an intimate metal-support interaction.

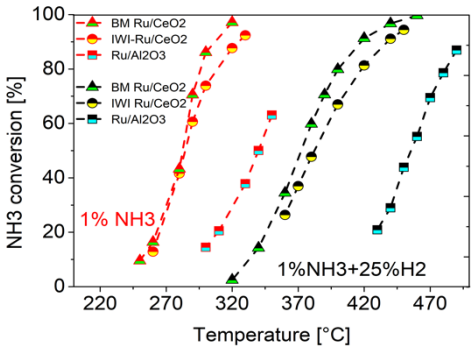


Figure 1. Catalytic activity comparison

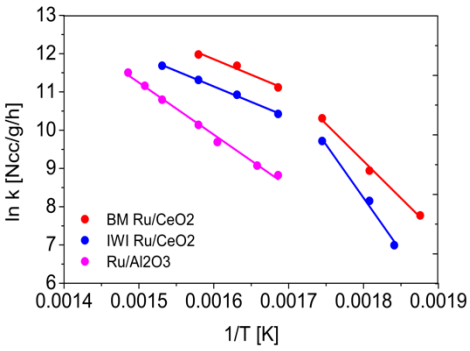


Figure 2. Arrhenius plots, 2.55% NH_3

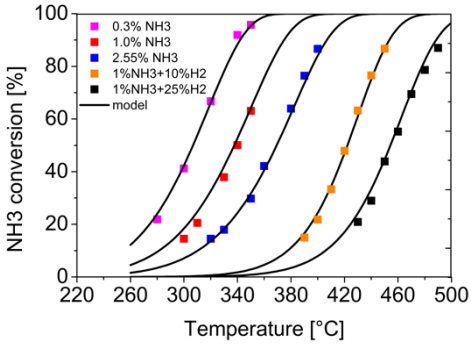


Figure 3. Experimental and modelled effects of NH_3 and H_2, Ru/Al_2O_3

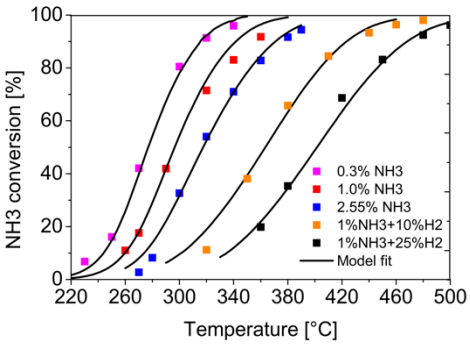


Figure 4. Experimental and modelled effects of NH_3 and H_2, Ru/CeO_2-IWI

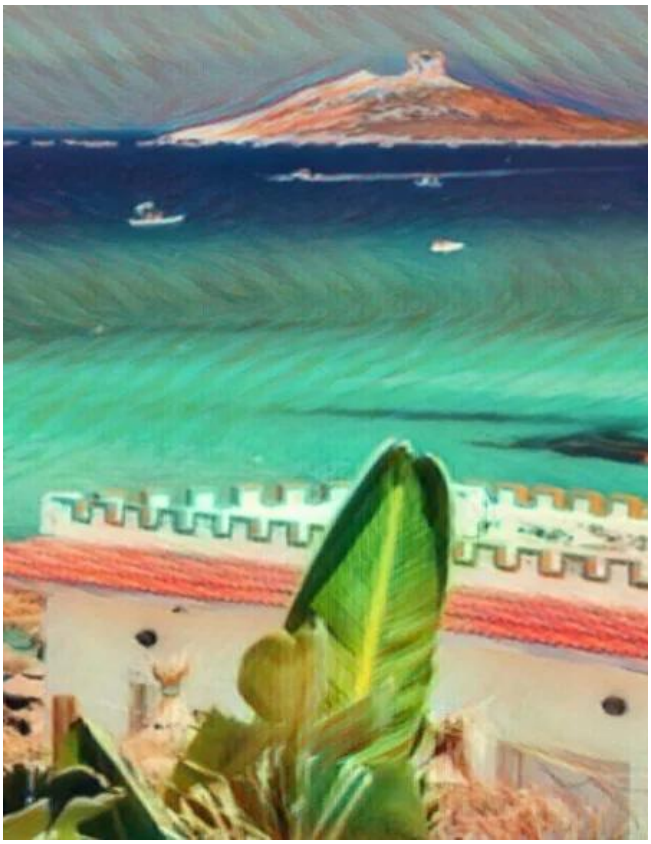
References

1. M.L.T. Triviño, S. Doi, Y.S. Kang, et al., *Chem Eng J* **2023**, *476*, 146715.
2. K. Yamazaki, M. Matsumoto, M. Ishikawa, et al., *Appl Catal B* **2023**, *325*, 122352.
3. J.H. Shin, U. Jung, J. Kim, et al., *Appl Catal B* **2024**, *340*, 123234.

Acknowledgements

The authors gratefully acknowledge the Grind-Ru PRIN 2022 and the financial support for Yi Qiu's doctoral study provided by the China Scholarship Council (CSC).

POSTER ABSTRACTS



Development of Catalyst Bed Concepts for Induction Heating for Emission Control

Asad ASADLI[*,1], Paolo DOLCET[2], Vishrant KUMAR[3], Alexis BORDET[3], Silvia GROSS[2], Moritz WOLF[1,4]
[1]*Karlsruhe Institute of Technology, Institute of Catalysis Research and Technology, Hermann-von-Helmholtz-Platz 1, Eggenstein-Leopoldshafen, Germany.*
[2] *University of Padova, Department of Chemical Sciences, Via Francesco Marzolo 1, Padova, Italy.*
[3] *Max Planck Institute of Chemical Energy Conversion, Stiftstrasse 34-36, Mülheim an der Ruhr, Germany.*
[4] *Karlsruhe Institute of Technology, Engler-Bunte-Institut, Engler-Bunte-Ring 7, Karlsruhe, Germany.*
**asad.asadli@kit.edu*

Significance and Relevance

Greenhouse gas emissions (GHGs) rise at alarming rates, making it crucial to address this issue. While 15% of the total emissions are accounted for by the transport sector, 60% come from the energy and chemical industry.[1] As the chemical industry moves toward electrification, traditional emission control technologies must be adapted to align with these emerging trends. This work demonstrates that electromagnetic induction heating technology can be applied to provide highly dynamic heating, e.g. for accommodating spontaneous emissions. Further, this technology supports industrial electrification by alternative heating of catalytic processes.

Preferred and 2nd choice for the topic: Catalysis to electrify the chemical production, automotive and stationary emission control
Preferred presentation: Poster

Introduction and Motivations

Electromagnetic induction heating is a promising candidate for achieving controlled, dynamic, and immediate heat regulation, which may contribute to industrial electrification when being coupled with chemical processes.[2] In the induction heating process, energy is converted into radiofrequency electromagnetic waves while susceptors release heat when they are immersed in an alternating magnetic field.[3] Modifying the active phase to serve as a susceptor for induction heating with specific magnetic susceptibility poses a challenge for emission control applications. However, effective heat dissipation near the active phase is expected to be similarly efficient for the chemical reaction. In a simplified approach, the catalyst bed can be adapted for induction heating using a physical mixture of susceptors and catalysts (Figure 1).

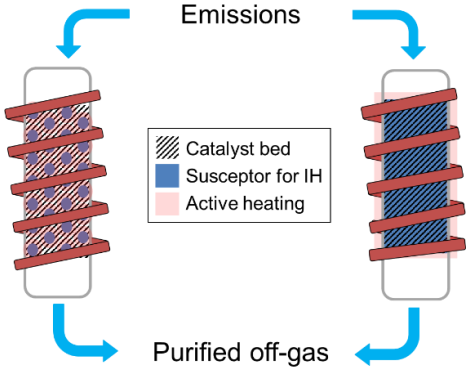


Figure 1. Schematic illustration of different catalyst bed concepts for emission control applications using induction heating (IH). Left – stainless steel beads as susceptors, right – powder of susceptor as part of the catalyst bed.

Materials and Methods

In this work, different catalyst bed concepts were developed by using a variety of susceptors for induction heating. On the one side, commercially available stainless steel beads (SS316) sized between 1 and 5 mm were utilized as susceptors. Aside from these bulk susceptors, mixed metal iron oxides (ferrites) containing cobalt and nickel were synthesized using co-precipitation, hydrothermal, or

surfactant-free methods, resulting in various particle sizes and magnetic properties.[4, 5] Additionally, Pt/Al_2O_3 is decorated with iron carbide nanoparticles (ICNP) via organometallic approach.[6] Susceptors with different size fractions were physically mixed with the Pt/Al_2O_3 to modify the catalyst bed and allow for emission control testing. In addition to induction heating studies, susceptors were thoroughly characterized and material properties were correlated with the bed temperature during induction heating. Here, magnetic characterisation of the susceptors becomes particularly important and has been conducted using X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Raman Spectroscopy, Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), magnetometry, and specific absorption rate (SAR) measurements.

Results and Discussion

The temperature in the catalyst bed can be adjusted by the supplied power, the ratio of catalyst-susceptor-SiC, the mixing homogeneity, size fractions, and other parameters. Overall, induction heating has demonstrated itself as a rapid and controllable technique, achieving an isothermal bed within 5-10 minutes, depending on the target temperature and materials used. Regarding the susceptors, nickel ferrites outperformed cobalt ferrites due to their lower coercivity. Meanwhile, large stainless and carbon steel beads demonstrated a faster heating, but performance degradation over time. Iron carbide decorated Pt/Al_2O_3 was found to have a faster magnetic response and owing to their smaller particle size they have shown a superparamagnetic induction heating behaviour. The herein presented preparative work provides a basis for currently running activity tests for the oxidation of CO as the first model reaction using induction heating.

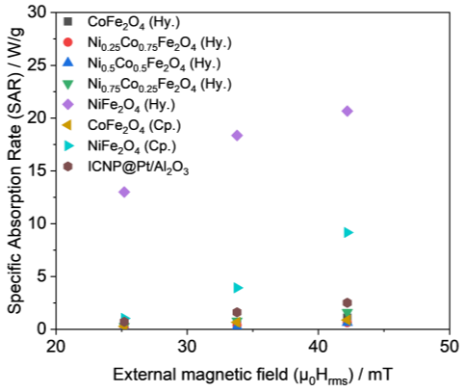


Figure 2 Specific absorption rates of synthesized susceptors.

References

1. W. F. Lamb, T. Wiedmann, J. Pongratz, R. Andrew, M. Crippa, J. G. J. Olivier, D. Wiedenhofer, G. Mattioli, A. A. Khourdajie, J. House, *Environ. Res. Lett.* **2021**, *16*, 073005.
2. W. Wang, G. Tuci, G. Duong-Viet, Y. Liu, A. Rossin, L. Luconi, J. Nhut, L. Nguyen-Dinh, C. Pham-Huu, G. Giambastiani, *ACS Catal.* **2019**, *9,* 7921.
3. H. Kreissl, J. Jin, S. Lin, D. Schüette, S. Störtte, N. Levin, B. Chaudret, A. Vorholt, A. Bordet, *Angew. Chem. Inter. Ed.* **2021**, *60,* 26639.
4. P. Dolcet, S. Diodati, F. Zorzi, P. Voepel, C. Seitz, B. M. Smarsly, S. Mascotto, F. Nestola, S. Gross, *Green Chem.* **2018**, *20*, 2257
5. M. Wolf, N. Fischer, M. Claeys, *Mater. Chem. Phys.* **2018**, *213*, 305

Acknowledgements

This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – SFB 1441 – Project-ID: 426888090. The Institute of Functional İnterfaces (IFG) and Prof. Dr. Matthias Franzreb are acknowledged for access to magnetometry. We thank DFG for financial support (INST 121384/73-1) and Prof. Dr. Jan-Dierk Grunwaldt (KIT) for providing access to Raman spectrometry.

Optimizing Performance of Ce/Zr/Pr-based Gasoline Soot Oxidation Catalysts by Mechanochemical Synthesis

Rizwan Asghar[1], Carla de Leitenburg[1], Rudy Calligaro[1], Alessandro Trovarelli[1]
[1]*University of Udine, DPIA, Udine, Italy*
asghar.rizwan@spes.uniud.it

Significance and Relevance

Mechanochemical synthesis is an environmentally friendly synthetic approach[1] that is solvent-free and is streamlined compared to other preparation methods. It is also capturing interest for the preparation of efficient heterogeneous catalysts[2]. In this work, mechanochemical synthesis was found to be promising for the synthesis of mixed rare-earth oxide formulations based on Cerium (Ce), Zirconium (Zr) and Praseodymium (Pr) with lower Pr amount respect to what previously reported in literature[3]. This was proven to be associated to the preparation methodology and to the presence of small amount of Zr into CePr which enhanced Oxygen ion mobility and led to improved catalytic activity.

Preferred topic: Automotive and stationary emission control
2nd choice: Air cleaning and combustion

Preferred presentation: *Poster*

Introduction and Motivations

Plug-in Hybrid Electric Vehicles (PHEV) equipped with Gasoline Direct Injection (GDI) engines are of great interest nowadays owing to their fuel efficiency and reduced CO_2 emissions. However, high PM emissions during cold start pose major confront for environmental implication. The combination of gasoline particulate filter with a catalyst is an effective approach for reducing the temperature of soot oxidation. Ceria-based catalyst, with their high OSC and redox cycle are the most studied and promising materials in the field of soot oxidation. Because of its poor thermal stability, ceria suffers from sintering and consequent loss of activity at elevated temperatures. For this reason, CeZr formulations can be used, since better thermal stability can be obtained[4]. The low oxygen content in the gasoline engine exhaust contributes to the difficulty of low temperature soot combustion. Therefore, the use of the highly reducible Pr can significantly improve catalytic performance by boosting the OSC for oxygen deficient environment. The aim of this work is to prepare some CeZrPr formulations to investigate the effect of Zr introduction into the CePr lattice and to explore the feasibility of a more sustainable synthetic approach, namely ball milling, which has the advantages of being solvent-less, faster and easy to scale up.

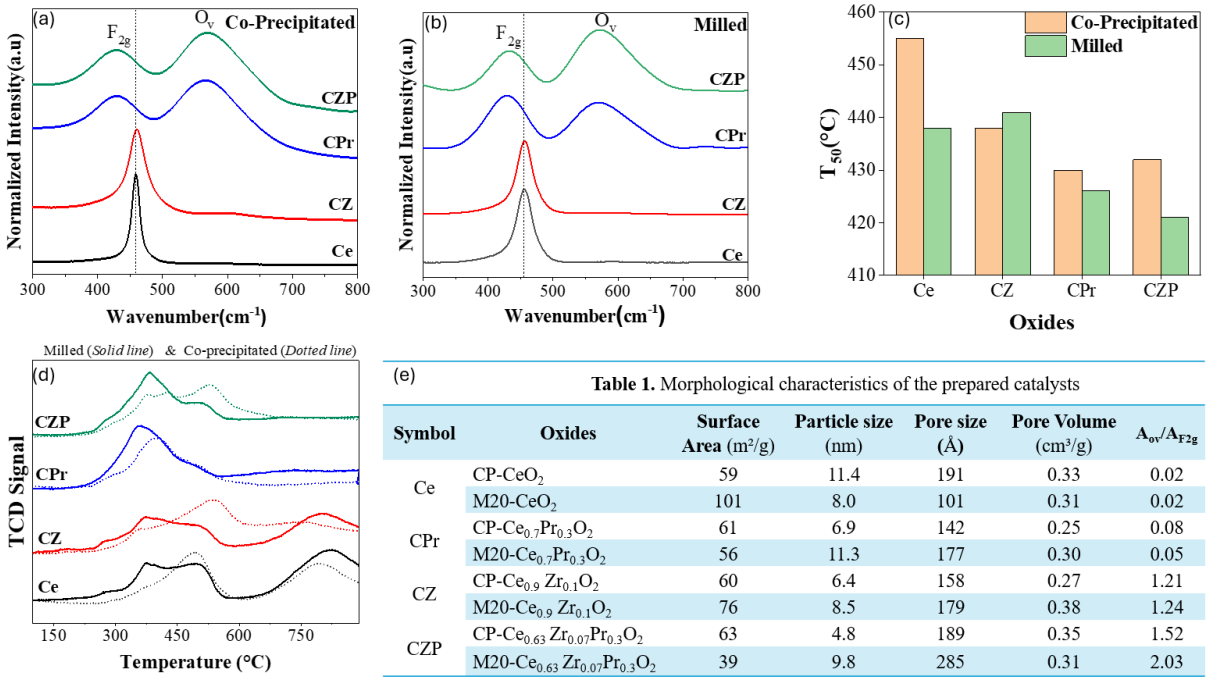
Materials and Methods

CeO_2, $Ce_{0.9}Zr_{0.1}O_2$, $Ce_{0.7}Pr_{0.3}O_2$, $Ce_{0.63}Zr_{0.07}Pr_{0.3}O_2$ were synthesized with mechanochemical synthesis starting from nitrate hydrate salts. The ratio of Ce/Zr was 9/1 for both CeZr and CeZrPr. The prepared samples were characterized using XRD, Raman spectroscopy, BET along with porosimetry measurements, and TPR for the evaluation of structural and catalytic properties. The prepared supports were mixed with commercial soot in a 4.7 wt.% loading and evaluated for soot oxidation activity by means of TGA under different environments (N_2, $1\%O_2/N_2$ and $20\%O_2/N_2$). The materials were compared with some analogues prepared via wet chemistry co-precipitation technique.

Results and Discussion

Both XRD and Raman analysis results support the solid solution formation for doped samples irrespective of the synthesis method. Raman analysis showed a shift and a widening of the F_{2g} peak at around $460cm^{-1}$ in the doped samples with respect to pure ceria (see Figure 1(a, b)) with a magnitude that depends on dopant cation. The appearance of band around 600 cm^{-1} (A_{ov}) is related to defects or oxygen vacancies present in the material. The intensity and width of the defect band increase moving

from Ce to CeZrPr and it was intense for Pr containing samples due to the easy reducibility of Pr. The ratio of the A_{ov}/A_{F2g} reported in Table 1 represents the ease of oxygen ion mobility[5]. This ratio was highest for milled CZP, which were expected to have excellent oxidation and reduction performance. This indication was in accordance with results of H_2 TPR (Figure 1(d)) and soot oxidation in 1% O_2(Figure 1(c)). Interestingly, the performance of milled samples was better than that of the co-precipitated counterparts for low temperature shift of either soot oxidation or H_2 reduction temperature. The better performance of milled CePr and CeZrPr, despite having lower surface area (Table 1), can be attributed to the higher concentration of reduced Pr. Overall, the optimized composition prepared by a mechanochemical approach coalesced in a single formulation the benefits of high OSC of Ceria, thermal stability of Zr and high catalytic activity of Pr in an oxygen deficient environment providing an effective catalysts for gasoline soot oxidation technology.



(e)

Table 1. Morphological characteristics of the prepared catalysts

Symbol	Oxides	Surface Area (m^2/g)	Particle size (nm)	Pore size (Å)	Pore Volume (cm^3/g)	A_{ov}/A_{F2g}
Ce	CP-CeO_2	59	11.4	191	0.33	0.02
	M20-CeO_2	101	8.0	101	0.31	0.02
CPr	CP-$Ce_{0.7}Pr_{0.3}O_2$	61	6.9	142	0.25	0.08
	M20-$Ce_{0.7}Pr_{0.3}O_2$	56	11.3	177	0.30	0.05
CZ	CP-$Ce_{0.9}Zr_{0.1}O_2$	60	6.4	158	0.27	1.21
	M20-$Ce_{0.9}Zr_{0.1}O_2$	76	8.5	179	0.38	1.24
CZP	CP-$Ce_{0.63}Zr_{0.07}Pr_{0.3}O_2$	63	4.8	189	0.35	1.52
	M20-$Ce_{0.63}Zr_{0.07}Pr_{0.3}O_2$	39	9.8	285	0.31	2.03

Figure 1: (a,b) Raman spectrum of milled (M20) and co-precipitated (CP) samples, (c) Temperature of 50% soot oxidation in 1%O_2 (d) Hydrogen temperature programmed reduction(H_2-TPR) profiles (e) **Table 1**: structural and textural properties of mixed oxides.

References

1 M. Danielis, S. Colussi, N. J. Divins, L. Soler, A. Trovarelli and J. Llorca, *Johnson Matthey Technology Review*, **2024**, *68*, (2), 217–231.

2 M. Danielis, A. Felli, M. Zampol, N. Fonda, P. Brüner, T. Grehl, E. Furlani, S. Maschio, S. Colussi and A. Trovarelli, *ACS Omega*, **2024**, *9*, 12046–12059..

3 S. Fahed, R. Pointecouteau, M. Aouine, A. Boréave, S. Gil, V. Meille, P. Bazin, O. Toulemonde, A. Demourgues, M. Daturi and P. Vernoux, *Applied Catalysis A General*, **2022**, *644*, 118800.

4 W. Chen, L. Fan, X. Jiang, J. Guo, H. Liu and M. Tian, *ACS Omega*, **2022**, *7*, 16352–16360.

5 J. C. Martínez-Munuera, M. Zoccoli, J. Giménez-Mañogil and A. García-García, *Applied Catalysis B*, **2019**, *245*, 706–720.

Acknowledgements

Finanziato dall'Unione Europea – NextGenerationEU - PNRR M4.C2.1.1 - PRIN 2022 – Codice 2022JRT7WZ – CUP G53D23001210006

DFT Insights and Experimental Evaluation of MnCeOx/HAP Catalysts for Efficient Phenol Degradation in CWAO

D. Bouazzi*[1,2], A. Cajumi[1,2], M. Samperi[2], F. Randazzo[2], G. Bonura[2], C. Cannilla[2], F. Arena[1,2]
[1]*Dipartimento di Ingegneria, Università degli Studi di Messina, Viale F. Stagno D'Alcontres 31, I-98166 S. Agata (Messina), ITALY.*
[2] *Istituto CNR-ITAE ''Nicola Giordano'', Via Salita S. Lucia 5, I-98126 S. Lucia (Messina), Italy.*
** e-mail corresponding: dorsaf.bouazzi@unime.it*

Significance and Relevance

Toxic organic pollutants such as phenols in industrial wastewater present significant environmental challenges due to their persistence and toxicity. Catalytic Wet Air Oxidation (CWAO) offers a sustainable approach, converting these pollutants into CO_2 and H_2O under mild conditions. This study investigates $MnCeO_x$ composite catalysts supported on hydroxyapatite (HAP) for Catalytic Wet Air Oxidation (CWAO) of phenol. These materials exhibit excellent activity, stability, and selectivity, achieving nearly complete phenol removal and efficient conversant CO_2 production under mild conditions. The novelty lies in the integration of HAP as a robust support with $MnCeO_x$, exploiting redox activity and oxygen activation to improve wastewater treatment efficiency.

Preferred and 2nd choice for the topic: Water treatement; Materials for Catalysis
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

$MnCeO_x$ catalysts are particularly promising, as their redox properties effectively enhance the degradation of organic compounds[1].
In this study, a novel synthesis procedure for $MnCeO_x$/HAP catalysts was developed to prepare materials characterized by high surface area, superior crystallinity, and excellent redox activity. The use of hydroxyapatite (HAP) enhances the dispersion and stability of the metal oxides. *Ex-situ* and *in-operando* characterization revealed the physicochemical features which represent the key factor for optimizing catalytic systems. The catalysts efficiency in phenol degradation highlights their potential for sustainable wastewater treatment.

Materials and Methods

A coupled redox-precipitation-impregnation route has been exploited to prepare Mn-based catalysts: this approach combines redox reactions for synthesizing MnCeOx followed by impregnation of hydroxyapatite (HAP) to form a composite material. Analytical, morphological, structural and surface properties were investigated by using XRF, XRD, SEM and TEM microscopy, N_2 adsorption/desorption, TGA-MS hyphenated measurements and Raman spectroscopy. *In operando* DRIFT-MS measurements were performed using an environmental chamber located inside IS50 Thermofisher Spectrometer coupled with a Mass Spectrometer. The catalytic performance in phenol degradation was evaluated in a stirred PTFE-lined autoclave at 150°C under oxygen pressures ranging from 0.1 to 1 MPa. Reaction progress and CO_2 selectivity were analyzed by MS-GC and TOC measurements. Additionallty, Density Functional Theory (DFT) calculations were performed to investigate the electronic properties of phenol and its degradation pathways[2].

Results and Discussion

The synthesis method for the novel $MnCeO_x$/HAP catalyst proved highly effective, producing a material with enhanced thermal stability, high surface area, excellent dispersion, and good crystallinity. The catalyst exhibited outstanding performance in phenol removal, achieving high selectivity with minimal intermediate formation and good stability under reaction conditions (T = 150°C, PO_2 = 0.9 MPa, ρ = 0.2). DFT insights provided a deeper understanding of the high catalytic activity in phenol degradation, highlighting the critical role of electronic properties, adsorption behavior, and oxidation mechanisms

in enhancing the catalysts performance for CWAO applications. Theoretical results have been supported by spectroscopic investigations to define the degradation pathways and main intermediates formed during the phenol conversion.

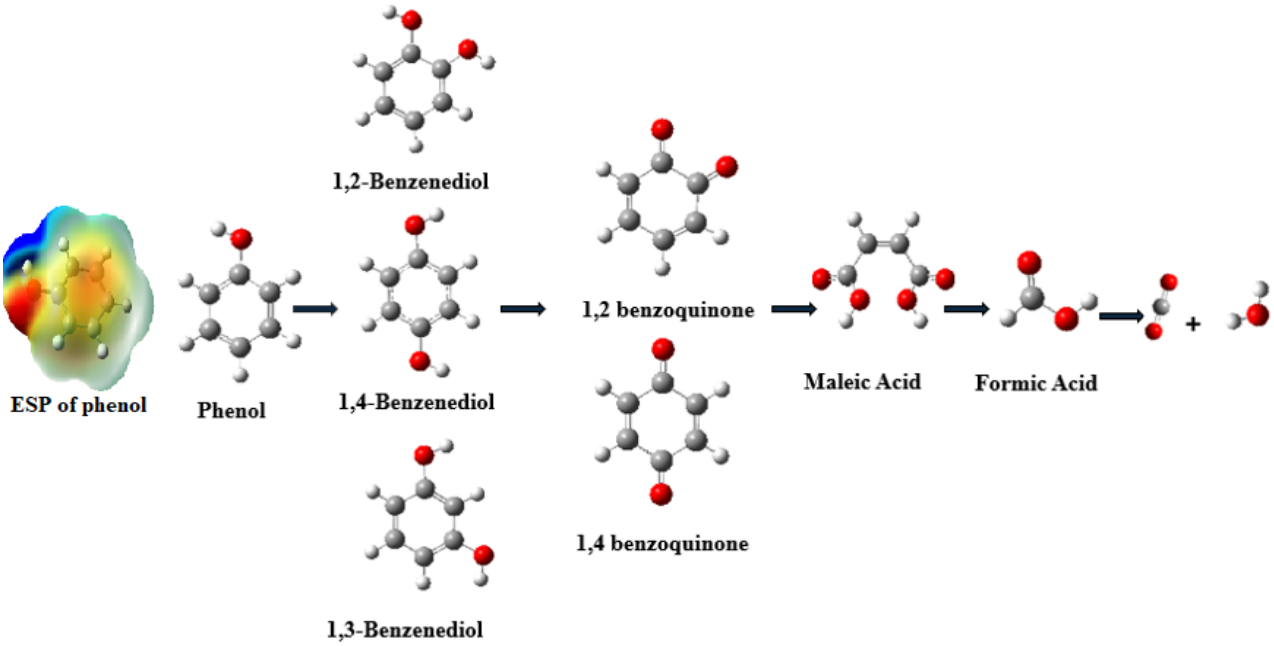


Figure 1: ESP map of Phenol and proposed degradation mechanism in CWAO in the presence of MnCeOx/HAP catalysts.

Conclusion:

$MnCeO_x$/HAP catalysts exhibit high activity and selectivity for phenol degradation under mild CWAO conditions. The synergistic redox properties of Mn and Ce play a critical role in achieving superior catalytic performance, whereas hydroxyapatite (HAP) enhances the dispersion and stability of the metal oxides, such catalysts resulting suitable for sustainable wastewater treatment.

DFT-derived Electrostatic Potential (ESP) map of phenol highlight regions of high electron density providing insights into reactive sites. Computational modeling further proposed a detailed degradation mechanism, elucidating the molecular pathways of phenol oxidation, confirmed by operando spectroscopic investigations.

References

1. P. Ma, N. Zhang, J. Shi, H. Lu, J. Fan, M. Li, Q. Deng, Z. Fang, B. Chen, Q. Zheng, S. Ye RSC advances, 2024, *RSC advances* 14.50 (2024) 37618-37627.
2. X. Jia, J. Zhang, Q. Huang, C. Xiong, H. Ji, Q. Ren, J. Huang, S. Chen, Z. Jin, J. Chen, W. Guo, Y. Ge, Y. Ding, Materials Research Bulletin 167 (2023) 112435.

Acknowledgements

This research was funded by PRIN 2022 - Missione 4 Componente 2 investimento 1.1 - D.D. 104 del 02-02-2022 Progetto AGROMET - 2022EX89KF CUP: B53D23005950006 - Next Generation EU - Bando FIS 2021- Fondo Italiano per la Ricerca – FIS00002427 SUPERBIO.

Recyclable Ni@Al_2O_3 catalyst for Dry Reforming of Methane

Rachele BRAIDO*[,1], Giulia DA PIAN,[1] Irene MARTIN,[2] Giuseppe CRUCIANI,[3] and Michela SIGNORETTO[1]

[1] *Department of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice, and INSTM RUVe Via Torino 155, 30172-Venezia, Italia*

[2] *Functional Nanosystems, Italian Institute of Technology (IIT), Via Morego 30, 16163 Genoa Italy, and Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 34, 10129 Turin Italy*

[3] *Department of Physics and Earth Science, University of Ferrara, Via Saragat 1, 44122-Ferrara, Italia*

* rachele.braido@unive.it

Significance and Relevance

A Ni@Al_2O_3 catalyst with a core-shell like structure was tested for Methane Dry Reforming (DRM). Studies suggest that protecting the metal's active site can prevent deactivation caused by sintering and coke deposition. In this study stability tests and several regeneration cycles were performed, demonstrating that the different catalytic structure obtained is suitable for DRM purposes.

Preferred and 2nd choice for the topic: H_2 storage and transportation, green H_2 production, hydrogen vectors, CO_2 utilization and recycling

Preferred presentation: Poster

Introduction and Motivations

Dry reforming of Methane is a catalytic reaction that converts two of the most impactful greenhouse gases - CH_4 and CO_2 - into syngas[1]. The reaction has not been applied yet at industrial level due to two major deactivation challenges: sintering of the metal active phase and coke deposition. The first one is related to the high temperature required by the reaction's endothermic nature. The second one is related to secondary side reactions[2]. To address the deactivation problems, the metal active site (Ni) can be surrounded by a metal oxide shell (Al_2O_3), which protects the Ni and provides a confinement effect.

Materials and Methods

The obtained catalyst was tested for the DRM reaction at 650 °C in a fixed bed reactor with a GHSV of 12000 h^{-1}, using a CH_4:CO_2:He ratio of 1:1:18, under a total flow of 200 mL/min. Additionally, recycling tests were conducted.

The fresh and spent samples were characterized using various techniques such as XRD, SEM, TEM, TPR, TPO, and N_2 physisorption.

Results and Discussion

The activity test demonstrated that the catalyst has an active and stable catalytic behaviour achieving a good H_2/CO ratio. In addition, the recycling test showed that the catalyst effectively converts the reactant gases into syngas, being stable for up to five redox cycles.

References

1. M. Pizzolato, G. Da Pian, E. Ghedini, A. Di Michele, F. Menegazzo, G. Cruciani, and M. Signoretto, *Reactions*, **2022**, *3*, 634 – 647.

2. M. Pizzolato, G. Da Pian, E. Ghedini, A. Di Michele, F. Menegazzo, G. Cruciani, and M. Signoretto, *Catalisys Today*, **2023**, *418*, 114041.

Development of Multi-Emission Fluorescent Carbon Dot-Polyester Composites for Application as Tracers in Recycled Polyester Textile Fibers

Wei-Yu Chen *
Department of Materials Engineering, National Pingtung University of Science and Technology, Pingtung, Taiwan R.O.C
** e-mail: wycehn@mail.npust.edu.tw*

Significance and Relevance

The research presents an innovative synthesis of multi-emission fluorescent carbon dot-polyester composites utilizing an *in-situ* polymerization method. This technique guarantees a uniform dispersion of sub-10 nm carbon dots, effectively addressing traditional challenges related to uneven dispersion and dust hazards. The composites, employed as tracers in recycled polyester fibers, exhibit unique excitation-dependent optical properties, facilitating precise traceability and the establishment of product history. This approach aligns with circular economy objectives, reduces production costs, and adheres to environmental standards, providing a groundbreaking, eco-friendly solution to enhance textile recycling and sustainability efforts.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion & Circular economy

Preferred presentation: Poster

Introduction and Motivations

This study addresses the significant challenges faced by the textile industry in light of global environmental pressures and carbon neutrality goals. As the fourth-largest polluting industry worldwide, the textile sector consumes approximately 109 million tons of fibers annually, resulting in substantial greenhouse gas emissions and waste generation. Traditional linear economic models lead to discarded textiles being sent to landfills or incinerators, causing severe environmental damage. With an increasing global emphasis on sustainable development and circular economy principles, there is a growing demand from international brands and consumers for recycled materials, such as polyester fibers. However, existing tracer technologies—including rare earth fluorescent materials, metal ions, and DNA tracers—while utilized in some applications in Europe and the United States, face limitations such as high costs, inadequate environmental performance, and complex production processes, which restrict their broader adoption in the textile industry.

This research presents a green, biopolymer-based *in-situ* polymerization method for synthesizing multi-emission fluorescent carbon dot-polyester composites. This one-step process ensures the uniform dispersion of sub-10 nm fluorescent carbon dots within polyester substrates, effectively addressing the challenges of uneven dispersion and industrial dust risks associated with traditional methods. By blending these composites with recycled polyester pellets and spinning them into fibers, the resulting tracer-enabled polyester fibers enhance material traceability, establish comprehensive product histories, and improve market competitiveness. Compliant with environmental regulations, this technology also reduces production costs while providing efficient tracer solutions characterized by water resistance, photothermal stability, and unique optical properties. The outcomes of this study will support Taiwan's textile industry in achieving technological independence, positioning it as a global leader in green manufacturing, and fostering its transformation toward a low-carbon, sustainable future.

Materials and Methods

This study developed multi-emission fluorescent carbon dot-polyester composites through a green and environmentally friendly process, utilizing bio-based precursors such as gelatin, ethylene glycol, and terephthalic acid. By employing in-situ polymerization at high temperatures (250–290°C) and low

pressure (2 torr), the method achieved a uniform dispersion of sub-10 nm fluorescent carbon dots within the polyester substrate. This one-step process effectively addressed the challenges of uneven dispersion and dust hazards associated with traditional multi-step blending techniques, while also reducing production costs and energy consumption. The resulting composites were blended with recycled polyester pellets and spun into fibers that exhibited excitation-dependent optical properties. These fibers, which functioned as tracers, underwent chemical alcoholysis and were analyzed using fluorescence spectrometry, Fourier-transform infrared spectroscopy (FT-IR), and high-resolution transmission electron microscopy (TEM). The analyses confirmed the uniform distribution and structural integrity of the fluorescent carbon dots. The fibers demonstrated excellent photothermal stability and wash resistance, making them ideal candidates for use as textile tracers.

Results and Discussion

This study successfully developed multi-emission fluorescent carbon dot-polyester composites to serve as tracers for recycled polyester textile fibers. Utilizing an innovative *in-situ* polymerization method at high temperatures (250–290°C) and low pressures (2 torr), the synthesis achieved a uniform dispersion of sub-10 nm fluorescent carbon dots (approximately 2.4 ± 0.2 nm) within the polyester matrix. This approach effectively addressed challenges such as uneven dispersion and dust hazards commonly associated with traditional multi-step blending methods. Fluorescence spectroscopy demonstrated excitation-dependent emission, with excitation wavelengths ranging from 280 to 420 nm and an emission peak at 415 nm. High-resolution transmission electron microscopy (TEM) and Fourier-transform infrared spectroscopy (FT-IR) analyses confirmed the structural integrity of the material, highlighting its potential as a textile tracer. Furthermore, the fibers exhibited excellent photothermal stability and wash resistance, maintaining effectiveness at concentrations of up to 50 ppm.

This technique significantly reduced production costs and increased fluorescence intensity by nearly fivefold (2200 a.u. compared to 450 a.u.) when compared to multi-step methods. Through blending and spinning processes, the composites were effectively mixed with recycled polyester pellets to produce tracer-enabled fibers. The results align with circular economy principles, enhancing the traceability of recycled polyester materials while complying with environmental regulations and supporting the textile industry's transition to carbon neutrality. This technology integrates green chemistry with advanced materials science, demonstrating substantial potential in textile recycling and sustainable development.

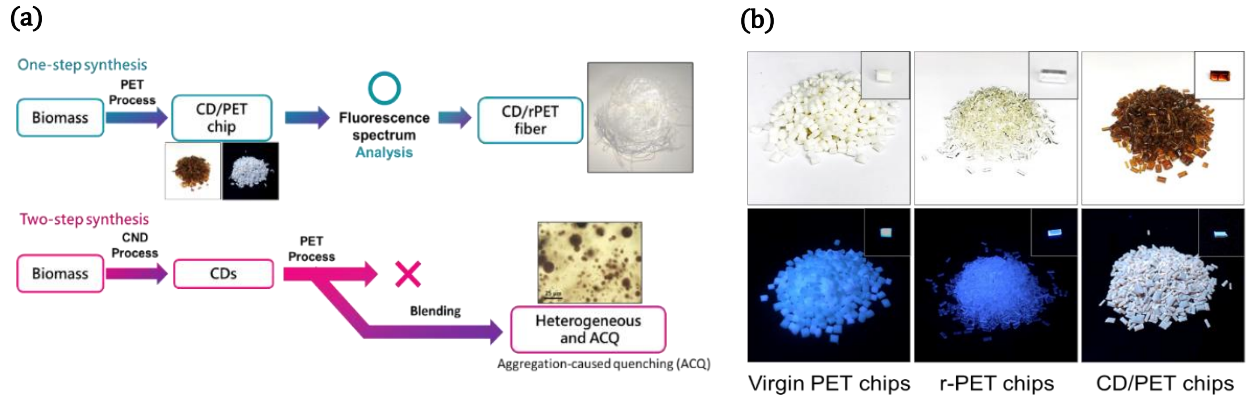


Figure 1. (a) Schematic Diagram of *In-Situ* Synthesis vs. Multi-Step Synthesis Strategies, (b) Visual representations of virgin polyester pellets, recycled polyester pellets, and fluorescent carbon dot-polyester composites are displayed under both daylight and ultraviolet light (365 nm excitation). Additionally, insets are included to showcase images of individual pellets.

Acknowledgements

We acknowledge the support of the National Science and Technology Council (NSTC) of Taiwan under grant NSTC 113-2113-M-020-002-.

Effect of catalyst composition on the activity and stability of Pt-Ni/ $MgAlO_x$ methane steam reforming catalysts

Andrea DE GIACINTO[1], Enrico TUSINI[1], Dmitry DORONKIN[1,2], Maria CASAPU[1], Jan-Dierk GRUNWALDT[1,2,*]

[1] *Karlsruhe Institute of Technology, Institute for Chemical Technology and Polymer Chemistry, Engesserstraße 18-20, 76131 Karlsruhe, Germany*

[2] *Karlsruhe Institute of Technology, Institute of Catalysis Research and Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*

** e-mail corresponding: grunwaldt@kit.edu*

Significance and Relevance

A series of mono- and bimetallic Ni/ and NiPt/$MgAlO_x$-based catalysts with different support compositions were prepared and tested for methane steam reforming during simulated daily startup and shutdown operation (DSS). The results obtained show a direct impact of the Ni:Pt and Ni:Mg/Al ratios on the catalyst activation/reactivation under methane steam reforming conditions. For certain catalyst compositions, formation of hardly reducible species was unraveled by *in situ* XRD and XAS investigations. Based on the knowledge gained, possible catalysts candidates for DSS were identified.

Preferred and 2nd choice for the topic: *1) H_2 storage and transportation, green H_2 production, hydrogen vectors, 2) Fundamental advances in understanding catalysis*
Preferred presentation: Short oral or poster

Introduction and Motivations

Steam reforming (SR) of methane is a well-established commercial process for generating approximatively 90% of the worldwide hydrogen production[1]. Ni-based catalysts are widely employed to produce H_2 in large-scale methane steam reformers under stationary conditions due to good price/performance ratio. Most of the applied catalysts are based on Ni/Al_2O_3, with high active metal loading (15-30%). To increase the stability against sintering and maintain Ni species dispersed, mixed oxides with tailored compositions can be exploited[2]. For domestic applications such as *in situ* H_2 production for fuel cells, where the power demand is varying on a daily basis, the SR reaction is conducted in a daily start-up/shut-down (DSS) operation mode. This approach exposes the catalysts to dynamic conditions, making Ni-based systems susceptible to oxidation and deactivation. Recent studies have shown that Ni oxidation to hardly reducible species can be prevented by adding small amounts of noble metals like Pt, Pd, Rh as catalyst dopants.[2,3] An alternative path is the tuning of the active metal-support interaction by adjusting the catalyst composition, which is systematically investigated in our study.

Materials and Methods

A series of samples with different Ni:Pt and Ni:Mg/Al ratios were synthesized and characterized by electron microscopy, XRD, H_2-TPR, and N_2-physisorption. Additionally, selected samples were studied by *in situ/operando* XAS and XRD measurements. Systematic CH_4 steam reforming tests were conducted in a plug-flow reactor. Besides performing several consecutive light-off/light-out activity tests, various atmospheres were applied to study the catalyst stability. An on-line FTIR spectrometer (Multigas FTIR, MKS) and mass spectrometer (Omnistar 320, Pfeiffer) were used for the analysis of the gas mixture at the reactor outlet.

Results and Discussion

The durability of the Ni-based mono and bimetallic catalysts was systematically investigated under dynamic reaction conditions. Various catalyst deactivation processes were induced by dynamic temperature and gas atmospheres variations (e.g. inert, steam-saturated inert, reaction mixture). Catalyst reactivation under reaction conditions was subsequently studied. For selected samples and conditions, the deactivation and reactivation processes were followed during *in situ/operando* XRD and XAS experiments. Pronounced changes in Ni state (oxidation state, particle size) were identified in

the deactivated catalysts, which could be correlated to the observed catalytic activity trends. As illustrated in Fig. 1, to withstand DSS operation, catalyst self-reactivation could be facilitated by the noble metal presence. Moreover, a careful adjustment of the support properties, e.g. metal-support interaction with Ni and/or the noble metal, prevents a fast drop in the catalyst activity under dynamic reaction conditions.

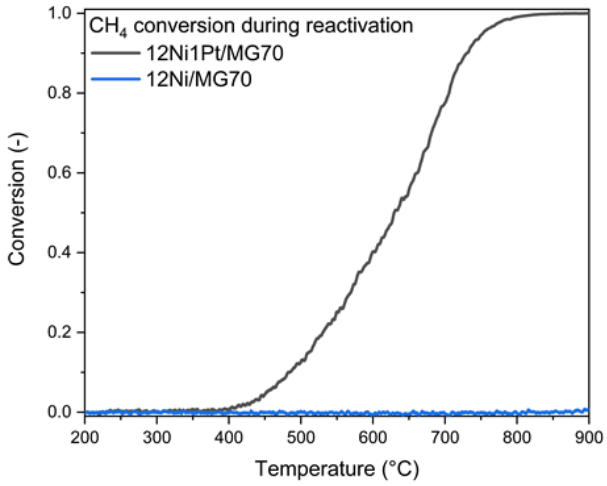


Figure 1: CH_4 conversion profile during reactivation of various catalysts following harsh deactivation.

References

1. I. Dincer, *Int. J. Hydrogen Energ.* **2012**, *37,* 1954-1971.
2. U. S. Mohanty, M. Ali, M. R. Azhar, A. Al-Zaseri, A. Keshavarz, S. Iglauer*, Int. J. Hydrogen Energ.* **2021***, 46,* 32809-32845.
3. E. Tusini, M. Casapu, A. Zimina, D. E. Doronkin, H. Stoermer, L. Barthe, S. Belin, J.-D. Grunwaldt*, ACS Catal.* **2024***, 14, 10,* 7463-7477.

Acknowledgements

This project has received funding from the European Union's Horizon 2020 Research and Innovation programme under the Marie Skłodowska-Curie Action – International Training Network (MSCA-ITN), grant agreement 813748.

Asymmetric ketones intermediates by cross-ketonization

Jacopo DE MARON*[,1], Gaetano Maria D'ONOFRIO[1], Tommaso TABANELLI[1], Andrea FASOLINI[1], Francesco BASILE[1], Fabrizio CAVANI[1].

[1]*University of Bologna, "Toso Montanari" Industrial Chemistry Dept., Viale Risorgimento 4, Bologna, Italy.*

** Jacopo.demaron2@unibo.it*

Significance and Relevance

This work demonstrates that the selective cross-ketonization of acid/asters can be exploited as a general synthetic approach to obtain valuable asymmetric ketonic intermediates with a continuous catalytic gas-phase process, thus avoiding the drawbacks of conventional homogeneously catalyzed, batchwise synthetic methods in the liquid-phase. This method achieved conversions of the limiting reactants between 75-85 %, selectivities in respect to the limiting reactants between 84-95 %, and space-time yields between 0.131-0.159 h^{-1}.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The usefulness of ketonization for the valorization of biomass-derived carboxylic acids (CA) is widely recognized. For instance, it has been recently proposed as a viable way to transform the volatile fatty acids (VFAs, C_4-C_8) obtained via fermentation of wet-waste (e.g., food waste, sewer sludge, animal manure) into sustainable aviation fuel (SAF) precursors[1]. Ketonization is also a promising way to produce valuable bio-based wax precursors by coupling the fatty acids (FAs) found in waste animal fat or vegetable oils (C_{12}–C_{18})[2]. However, despite the recent advance in ketonization-based processes to produce renewable fuels and oleochemicals, the full potential of this reaction has yet to be suitably exploited for the selective synthesis of high added-value chemical intermediates for the pharmaceutical, cosmetic and food industry. As of now, asymmetric ketones containing aromatic moieties are mainly produced by liquid-phase batch processes that co-produce significant amounts of waste (e.g., Friedel-Crafts, Heck, Suzuki, Grignard, Claysen-Schmidt, oxidations with peroxides)[3], while the examples of selective cross-ketonization of CAs or esters are relatively scarce[4]. Recently, the synthesis of acetyl furan (AF, a food additive and intermediate in the synthesis of antibiotics) via cross-ketonization between methyl 2-furoate (2-MF) and acetic acid (AA) (both obtainable from renewable resources) was proposed as a more sustainable alternative to conventional synthetic methods[5].

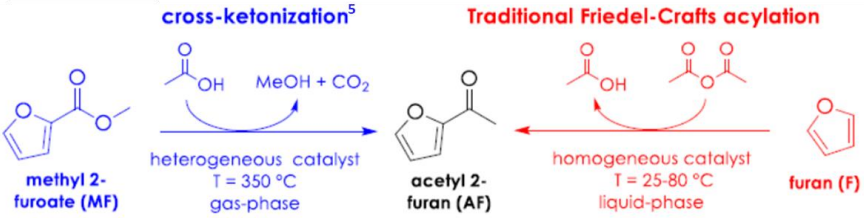


Figure 1 comparison between the gas-phase cross-ketonization pathway towards acetyl furan and the traditional Friedel-Crafts synthesis in the liquid-phase.

Starting from these seminal results, in this work the substrate scope of the gas-phase cross-ketonization approach was further demonstrated by targeting several valuable asymmetric ketones intermediates widely used as chemical intermediates, flavors/fragrances or pharmaceutical precursors (e.g., acetophenone, 4-methyl acetophenone, propiophenone, valerophenone, dihydrochalcone).

Materials and Methods

Catalytic runs were carried out in a gas-phase plant operating at atmospheric pressure over 1 cm^3 of catalyst pellets (30-60 mesh). Reactants were mixed in the desired molar ratio and fed with a volumetric pump into a stainless-steel line to be vaporized before the catalytic bed. The LHSV and the flow of N^2 carrier were adjusted to obtain the desired molar fractions in the gas-phase maintaining a

contact time t (at reaction temperature) = 1 s. The effluent from the reactor was condensed in a cold trap filled with acetonitrile and kept at 0 °C and analyzed offline with an Agilent 5890 Series II GC instrument (internal standard = dodecane, capillary column: DB-1701, 25 m × 530 µm × 1.05 µm). The effluent from the cold trap was analyzed online by means of GC-TCD (columns: Agilent CP-Molsieve 5A capillary column, 25 m × 530 µm × 50 µm and an Agilent CP-Silica PLOT, 30 m × 530 µm × 6 µm). Ceria (CeO_2, 193 m^2/g) was a commercial reference material (Rhodia Actalys HAS 5) and was calcined at 5 °C/min up to 400 °C for 4 h before use; zirconia (ZrO_2, 55 m^2/g), ceria–zirconia (Ce/Zr/O, 123 m^2/g) and lantania (La_2O_3, 26 m2/g) were synthesized by means of precipitation and co-precipitation, adapting a method from the literature[6], and calcined at 5 °C/min up to 550 °C, 400 °C, and 750 °C respectively. Catalysts were characterized by means of BET, XRD, TGA, Raman and TPR.

Results and Discussion

Catalytic runs were initially carried out at 350 °C and with a contact time equal to 1 second by vaporizing the feed in N_2 carrier to obtain a total organic concentration of 2 % in the gas-phase. ZrO_2 exhibited a higher catalytic performance and stability with respect to other well-known ketonization catalysts (e.g., CeO_2, Ce/Zr/O and La_2O_3) in the synthesis of dihydrochalcone (HC) from ethyl 3-phenyl propionate (EPP) and ethyl benzoate (EB), in analogy with previous results obtained in the coupling of methyl 2-furanoate and acetic acid towards acetyl furan[5]. A detailed investigation of the process condition showed that the main parasitic reaction, i.e. the undesired homo-ketonization of EPP towards 1,5-diphenyl propanone, could be avoided either by increasing the EB/EPP molar ratio in the feed or by increasing the reaction temperature from 350 °C to 400 °C; the latter finding could be explained by the higher reactivity of EB at higher temperature. Once optimal reaction conditions were identified for the synthesis of acetyl furan (model aryl-alkyl ketone) and dihydrochalcone (model aryl-alkylaryl ketone), the synthetic method was scaled up to a feed containing 20 % total organic reactants and extended to the synthesis of the valuable compounds listed in Figure 2.

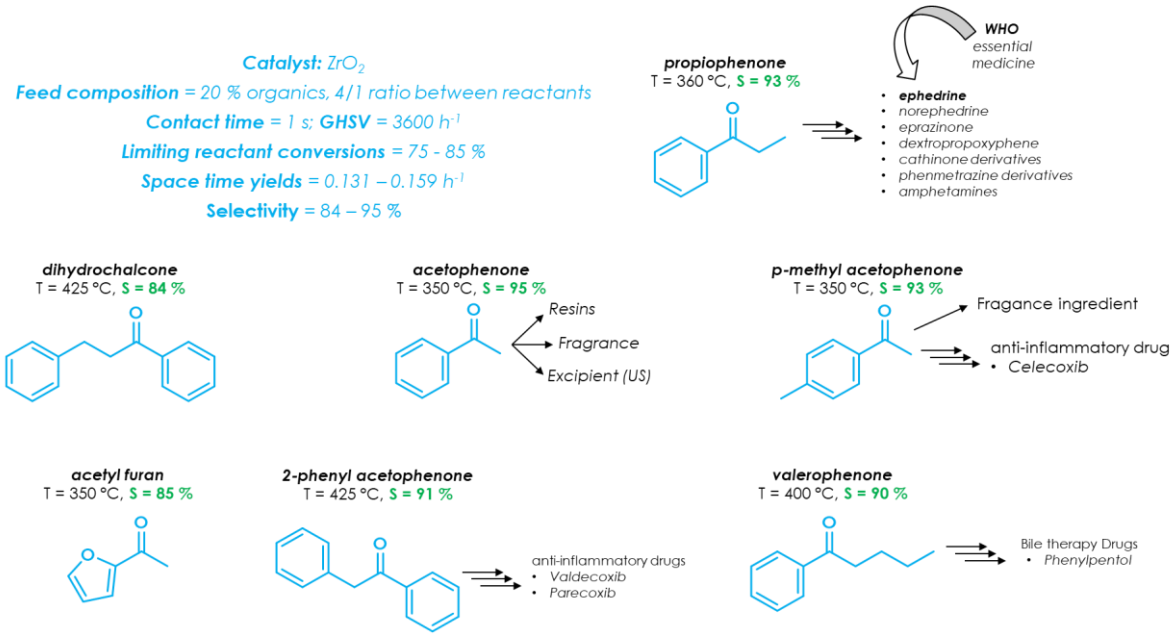


Figure 2 Substrate scope of the cross-ketonization synthetic approach.

References

1. J.H. Miller *et al.*, *Industrial & Engineering Chemistry Research* **2022**, *61*, 2997.
2. B. Boekaerts, *et al.*, Green Chemistry**2021**, *23*, 7137.
3. C. Zhuang *et al.*, *Chemical Reviews* **2017**, *117*, 7762.
4. T. Goculdas *et al.*, *Green Chemistry* **2023**, *25*, 614.
5. J. De Maron *et al.*, *Green Chemistry* **2023**, *25*, 7381.
6. J. De Maron *et al.*, *Sustainable Chemistry* **2022**, 3, 58.

Tailoring Active Sites Towards High Selectivity for Paired-Electrochemical Biomass Upgrade over Medium/High-Entropy Sulfide Aerogels

Bezawit Z. Desalegn, and Jeong Gil Seo*
Hanyang University, Department of Chemical Engineering, 04763, Seoul, South Korea.
Hanyang University, Clean-Energy Research Institute, 04763, Seoul, South Korea.
* jgseo@hanyang.ac.kr

Significance and Relevance

Multi-element [Medium (MES) and High-entropy (HES)] sulfide aerogels were successfully synthesized for the first time via a simple sol-gel method followed by supercritical drying and solid-gas phase sulfurization at a relatively low temperature. With successive addition of each metal a change in specific surface area, acidic/basic sites and adsorption orientation of substrates/intermediates was observed with significant implications to performance descriptors for electrochemical furfural upgrade. A direct relationship between the nature and number of acidic/basic sites is discovered for both selectivity (100%) and yield (85%) towards furoic acid, moving from mono-metallic to high-entropy systems.

Preferred and 2nd choice for the topic: Preferred: *Catalysis to electrify the chemical production/**2nd choice**: Green chemistry and biomass transformation, renewable resources conversion.*
Preferred presentation**:** *Oral preferred or Short Oral*

Introduction and Motivations

Severe environmental problems due to expedited technological advancements along with the gradual depletion of fossil fuel resources have initiated a surge in the utilization of renewable and abundant lignocellulosic biomass to produce sustainable, valuable, functional, and fine chemicals.[1] Furanic derivatives are substrates of prime interest as they represent a synthetic platform for numerous value-added compounds. Drop-in biofuels can be produced by reduction [hydrogenation/hydrodeoxygenation], while partial oxidation can yield various fine chemicals.[2] However, the conventional thermocatalytic process for the generation of platform chemicals requires extremely harsh reaction conditions, including high pressure, high temperature, and the use of external oxidants and reductants, which fueled the need for the development of greener conversion technologies. In this regard, electrochemical biomass upgrade, benefiting from room temperature/pressure operations with in-situ generated oxidations/reductants along with the advantage of controlling selectivity via voltage/electrolyte adjustments is gaining increased attention. However, due to the co-existence of various unsaturated functional groups in biomass feedstocks, selective transformation is a highly challenging task[3] that requires the design of task oriented, densely packed and synergistic active sites. Accordingly, in this work an array of MES/HES aerogels with unique inherent properties were synthesized and utilized as highly active electrodes for the paired electrochemical furfural upgrade.

Materials and Methods

The medium and high-entropy sulfide aerogels were synthesized via a two-step method. Specifically, wet gels with different metal combinations were prepared via a sol-gel method followed by CO_2 supercritical drying to obtain the high-entropy oxide aerogels, which were subjected to solid-gas sulfurization with elemental sulfur to obtain the final high-entropy sulfide aerogels. Electrochemical oxidation and reduction reactions were conducted in an H-type electrochemical cell separated by an anion exchange membrane, with graphite rod as the counter electrode, saturated Ag/AgCl as the reference electrode and the as-prepared aerogels drop-casted on nickel foam as working electrodes. 50mM furfural dissolved in 1M KOH was used as the anolyte and catholyte for anodic and cathodic reactions, respectively. The conversion, selectivity, yield and FE% were calculated by quantifying the products using high performance liquid chromatography (HPLC).

Results and Discussion

A progressive increase in conversion, selectivity, yield and FE% was observed with successive addition of metals. The mono-metallic sulfide aerogels (FeS_2 AG and NiS_2 AG) exhibited higher conversion for furfural with negligible selectivity towards the target product while the bimetallic sulfide [$FeNiS_y$ AG] showed the highest conversion along with increased furfuryl alcohol conversion. Interestingly, the incorporation of Cu to the bimetallic sulfide aerogel resulted in a significant improvement in selectivity, more specifically for electrodes where Cu replaced Fe ($Fe_{1.5}Ni_{2.5}CuS_y$ AG). Consecutively, the addition of Co ($Fe_2Co_1Ni_5Cu_2S_y$ AG [MES-Co]) to the trimetallic sulfide resulted in the highest selectivity of 98% towards furoic acid while maintaining conversion. Lastly, the incorporation of Zn to the MES-co ($Fe_2Co_1Ni_4Zn_1Cu_2S_y$ AG [HES-Zn])resulted in a 100% selectivity and the highest FA yield of 85%. It is believed that with successive addition of elements/metals the adsorption orientation of furfural was modified from a parallel to tilted and finally to a vertical configuration which favors the selective activation of the C=O bond and the formation of carboxylic acid by the nucleophilic attack of C=O with OH^- (**Figure 1**).

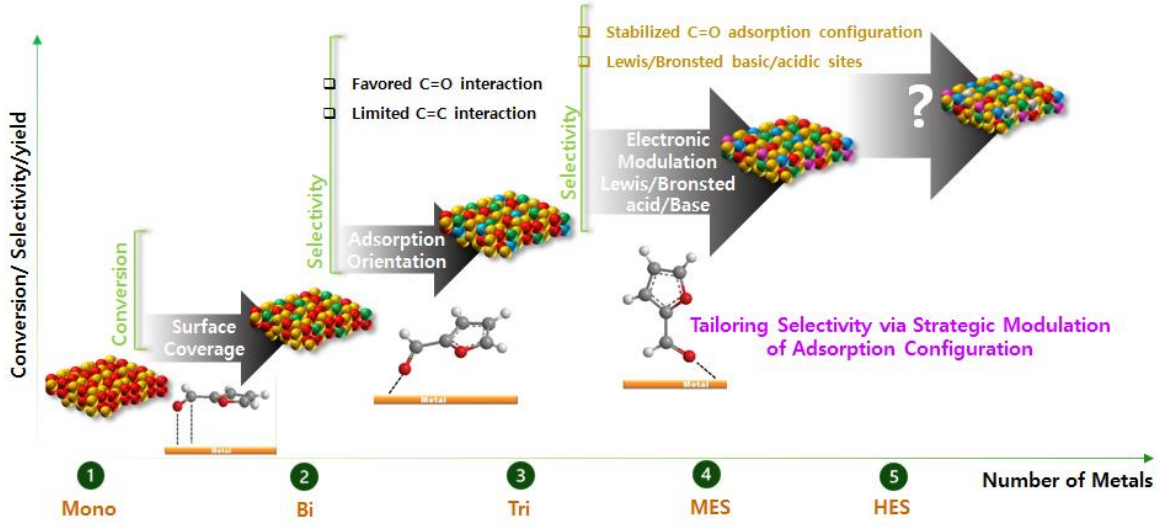


Figure 1 Schematic illustration of the effect of addition of metals on the adsorption orientation and performance descriptors of furfural towards furoic acid.

The presence of multi-component, adjacent and synergistic active sites is believed to bring forth systematic modifications in surface coverage, adsorption orientation, electronic modulation, and Lewis's acid-base pairs leading to improved conversion, selectivity and yield.

References

1. H. Wu, J. Song, H. Liu, Z. Xie, C. Xie, Y. Hu, X. Huang, M. Hua and B. Han, *Chem. Sci.*, 2019, **10**, 4692-4698.
2. B. You, X. Liu, N. Jiang and Y. Sun, *J. Am. Chem. Soc.*, 2016, 138, 13639–13646.
3. S. Liu, R. Tu, K. Liang, Y. Sun, X. Fan, J. Hu, H. Yang and X. Xu, *Fuel Process. Technol.*, 2023, **252**,107976.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (No. 2022R1I1A1A01064469).

Biodiesel improvement by skeletal isomerization on hierarchical zeolites

Jonathan Fabian SIERRA-CANTOR[1], Olinda GIMELLO[1], Luca BERNARDI[2,3], Anne AUBERT-POUËSSEL[1], Carlos-Alberto GUERRERO-FAJARDO[4], Francesco DI RENZO*[,1], Nathalie TANCHOUX[1], Corine GÉRARDIN[1]
[1] *Université de Montpellier-CNRS-ENSCM, ICGM, Montpellier, France.*
[2] *Alma Mater Studiorum Università di Bologna, Dip. Chimica Industriale "Toso Montanari", Bologna, Italy.*
[3] *Alma Mater Studiorum Università di Bologna, C[3] Center for Chemical Catalysis, Bologna, Italy.*
[4] *Universidad Nacional de Colombia, Departamento de Quimica, Bogotá, Colombia.*

Significance and Relevance

Biodiesel worldwide production is still rising and will do so for many years, as the delays of electrification of the fuel production for heavy-duty transport justify an intermediate introduction of bio-based renewables. Shift to continuous-flow processes and improvement of the properties of enoic esters from vegetable or recycled oils require new custom-tailored heterogeneous catalysts.[1]

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, Renewable resources conversion
Preferred presentation: Poster

Introduction and Motivations

The recrystallization of zeolites in cetyltrimethylammonium (CTA) solution is an accepted method to open a hierarchical micro-mesoporous network and improve the accessibility of the active sites.[2] Micro-mesoporous hierarchical zeolites can provide significant improvements in selectivity and stability of the methyl oleate isomerization in flow reactors, overcoming previously observed site passivation.[3]

Materials and Methods

Parent ferrierite (FER-PAR, Si/Al 9.7, BET surface area 394 m^2g^{-1}, αS external surface area 15 m^2g^{-1}) and dealuminated faujasite (Y30-PAR, Si/Al 30, BET 716 m^2g^{-1}, αS 110 m^2g^{-1}) were proton exchanged, recrystallized in cetyltrimethylammonium (CTA) solution, and calcined at 550°C, obtaining recrystallized FER-REC (Si/Al 6.6, BET 427 m^2g^{-1}, αS 159 m^2g^{-1}) and Y30-REC (Si/Al 24, BET 837 m^2g^{-1}, αS 583 m^2g^{-1}) catalysts that were tested for methyl oleate isomerization in batch autoclave (solventless, 285°C, 6 h) or in continuous flow reactor (285°C, N_2 flow, WHSV 3.5 h^{-1}).

Results and Discussion

The CTA recrystallization treatment has been applied to two kinds of zeolites with different microporosity - 10-member ring (10MR) medium size-micropore ferrierite and 12MR large-micropore high-silica faujasite - producing different structural mesoporosity in the two kinds of zeolites, with formation of MCM-41-like wormlike mesopores in faujasite and opening of a constrained negative-crystal mesoporosity in ferrierite (see Fig. 1A).[4,5]

Results of methyl oleate skeletal isomerization at 285 °C over faujasite and ferrierite catalysts are reported in Fig. 1B and 1C, respectively. In batch experiments (color bars in the figures), the yield of branched isomers on the parent zeolites was 27% on Y30-PAR and 55 % on FER-PAR. The difference between the two kinds of zeolites depends more on the shape selectivity of ferrierite for alkene isomerization than on the different amount of Brønsted acid sites. CTA recrystallization induces a limited yield improvement of 2% for Y30-REC and 4 % for FER-REC. In the case of the flow reactor experiments (lines with dots in Fig.1B and 1C), the yield of branched products on the parent zeolites is always lower than in the batch experiments and rapidly decreases with time-on-flow, until 4 % on Y30-PAR and 8 % on FER-REC after 7 h. When the recrystallized catalysts are used, the distribution of products on the two zeolites is completely different. In the case of faujasite Y30-REC (Fig. 1B, line b), the recrystallization induces a moderate improvement of yield and does not prevent a severe deactivation, reaching 9 % at 8 h time-on-flow. In the case of FER-REC (Fig.1C, line d), the yield of

branched monoenoic methyl esters rapidly rises to 53% and remains stable around this value for 8 h time-on-flow, at 98 % oleate conversion.

It has been surmised that the better results obtained on recrystallized ferrierite catalysts are due both to the well-known shape selectivity of the ferrierite structure for alkene isomerization reactions and to the solvent effect of condensed liquid phase in the constrained mesoporosity. It is likely that the condensate in the constrained porosity of FER-REC exert a washing effect on the poisoning deposits on the active sites, in a similar way of the effect of the pressurized liquid phase in the batch reactor experiments.

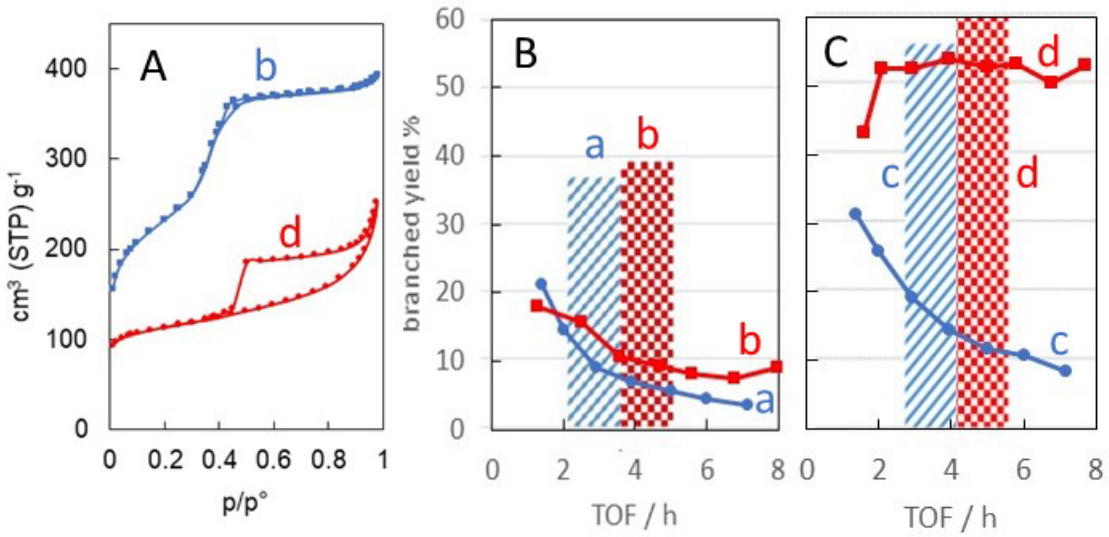


Figure 1 N_2 sorption isotherms for recrystallized samples (A) and branched isomer yield on faujasite (B) and ferrierite (C) catalysts (bars are batch results whereas lines and dots are continuous flow results vs. time-on-flow) Y30-PAR (a), Y30-REC (b), FER-PAR (c) and FER-REC (d).

Moreover, the higher continuous-flow methyl oleate isomerization on ferrierite induced a significant improvement of the cold-flow properties of the products, with freezing points on average 8 °C lower than for faujasite catalysts.

It appears that the limitations of catalyst stability in continuous flow process can be overcome by coupling the well-known shape selectivity of ferrierite for olefin isomerization with a mesopore shape able to provide an adsorbed liquid-mimicking phase. A correct choice of both micropore and mesopore architecture of hierarchical zeolites provides significant improvements in selectivity and stability of the methyl oleate isomerization in flow reactors.[3]

References

1. R. Maghrebi, M. Buffi, P. Bondioli, D. Chiaramonti, *Renew. Sustain. Energy Rev*. **2021**, *149*, 111264.
2. R. Chal, C. Gérardin, M. Bulut, S. Van Donk, *ChemCatChem*, **2011**, *3*, 67-81.
3. J. F. Sierra-Cantor, O. Gimello, C.-A. Guerrero-Fajardo, F. Di Renzo, H. Petitjean, M. Rivière, C. Gérardin, N. Tanchoux, *Appl. Catal. B: Environ*. **2024**, *344*, 123602.
4. R. Chal, T. Cacciaguerra, S. Van Donk, C. Gérardin, *Chem. Comm*. **2010**, *46*, 7840-7842.
5. X. Cheng, T. Cacciaguerra, D. Minoux, J.-P. Dath, F. Fajula, C. Gérardin, *Micropor. Mesopor. Mat.* **2018**, *260*, 132-145.

Promoted lanthanum oxysulfates as regenerable catalysts for soot oxidation in GPFs

Elisabetta M. CEPOLLARO[1], Stefano CIMINO[1], Michele E. FORTUNATO[1], Luciana LISI[*,1]
[1]*Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili (STEMS) – CNR, P.le Tecchio 80 – 80125 Napoli, Italy.*
** luciana.lisi@cnr.it*

Significance and Relevance

The temperatures of exhaust emissions from gasoline engines are higher than from diesel engines but the very low level of O_2 represents a critical issue for soot combustion.
Metal promoted lanthanum oxysulfate was proposed for the first time as possible catalyst to cover the high temperature range of soot oxidation in Gasoline Particulate Filters (GPF). This catalyst can reversibly use its lattice oxygen, completely turning into oxysulfide, to effectively oxidize soot to CO_2 also under inert flow and restoring the original oxysulfate structure even under very low O_2 levels, typical of emissions from a gasoline fueled engine.

Preferred and 2nd choice for the topic: Automotive and stationary emission control
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Gasoline Direct Injection (GDI) engines although more efficient than Port Fuel Injection (PFI) ones, produce a large amount of soot in the fuel-rich areas thus requiring the use of Gasoline Particulate Filter (GPF). Although the exhaust temperatures of a GDI (from 400 to 700 °C) are potentially high enough for homogeneous soot oxidation on the GPF, the very low level of O_2, due to the stoichiometric fuel combustion, represents a critical issue along with the almost complete absence of NO_2 removed in the upstream Three Way Catalyst (TWC)[1]. Moreover, in hybrid electric vehicles, despite their good fuel economy, the alternate switch between battery and internal combustion engine can cause soot emissions even higher than from vehicles without any electrification.
Lanthanum oxysulfate has a high Oxygen Storage Capacity (OSC) coupled to a very good thermal stability and cyclability that can potentially represent key-features for a catalyst which should operate under these severe conditions[2].
Promoted $La_2O_2SO_4$ has been investigated for the first time as potential high-temperature soot oxidation catalysts to be used in catalyzed GPFs.

Materials and Methods

Lanthanum oxysulfate was obtained by thermal decomposition of $La_2(SO_4)_3$ by heating it at 1000 °C for 2 h under He flow. Portions of $La_2O_2SO_4$ were impregnated with copper, cobalt or cerium by impregnation of the corresponding nitrate salts.
Soot oxidation experiments were carried out in a thermobalance coupled to a mass spectrometer (TG-MS) either under inert (Ar) or under 1% O_2/Ar flow. Materials were characterized before and after the soot combustion by ICP-MS, XRD, TEM and porosimetric analysis.

Results and Discussion

The TG-MS results showed that, despite the solid state of soot, its reaction with $La_2O_2SO_4$ deeply affected the onset temperature of the reduction to La_2O_2S under inert atmosphere. Specifically, the oxidation of carbon soot promoted the extraction and consumption of the lattice oxygen species from $La_2O_2SO_4$, which otherwise does not spontaneously release O_2. Nevertheless, for the unpromoted oxysulfate the undesired irreversible decomposition into lanthanum oxide, associated with the emission of SO_2, occurred.
This is effectively inhibited by the small addition of cobalt, copper or cerium to the catalyst, which not only effectively promoted the lattice oxygen mobility of the material, favouring the selective combustion of soot in the absence of O_2 starting from 630 °C, but totally inhibited the decomposition

with emission of SO_2, as shown in Fig.1. CeO_2, typically used in DPFs under excess oxygen, did not activate soot oxidation under inert atmosphere. Under 1% O_2, soot combustion was catalyzed by the active surface oxygen starting from temperatures as low as 400 °C, but at T≥ 630 °C the high OSC of the promoted lanthanum oxysulfate greatly boosted soot oxidation. When all carbon soot was burnt, the lanthanum oxysulfide phase produced by the reaction was completely reoxidized to the original $La_2O_2SO_4$ phase by the O_2 in the gas even at so low partial pressures, thus restoring the original catalyst.

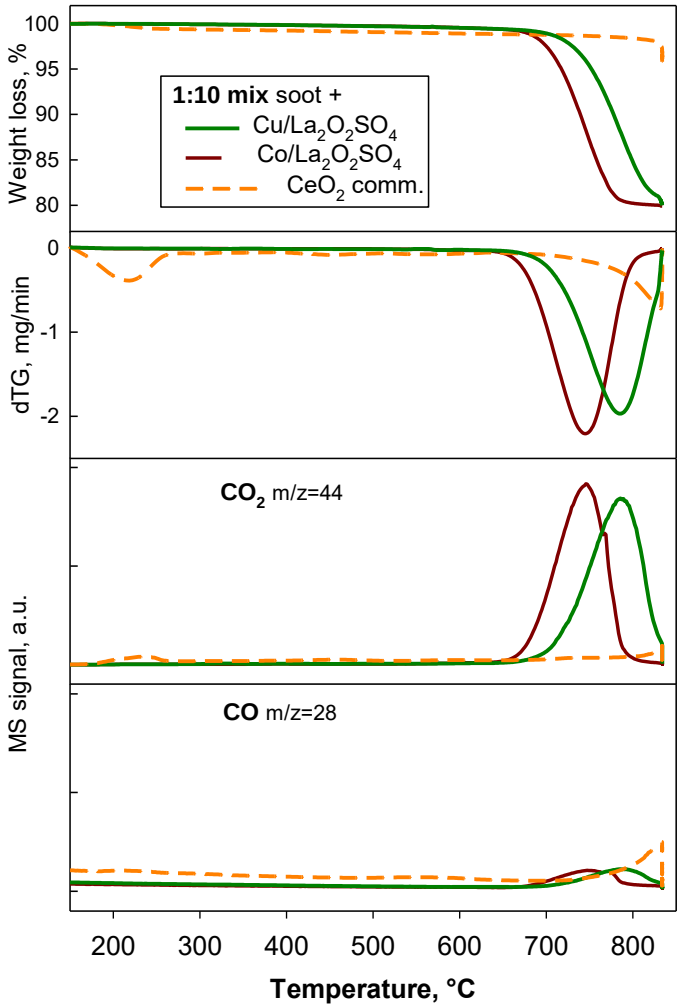


Figure 1 TG-MS analysis under inert flow for 1:10 mixtures of soot with metal (Cu, Co) promoted $La_2O_2SO_4$ compared to reference CeO_2: weight losses and corresponding derivative profiles and MS signals for CO_2 (m/z = 44) and CO trace (m/z = 28).

References

1. B. Giechaskiel, A. Melas, V. Valverde, M. Otura, G. Martini, *Catalysts* **2022** *12*, 70
2. S. Cimino, G. Mancino, L. Lisi, *Catalysts* **2019**, *9*, 147

Acknowledgements

This research was funded by European Union – Next Generation EU, Mission 4 Component 1 CUP B53D23006090006.

Gold nanoparticles on manganese oxides with different crystalline structures: enhancing low-temperature air pollutants abatement

Nadia GRIFASI[1], Francesca LIUZZI[2], Eleonora CALI'[1], Samir BENSAID[1], Nunzio RUSSO[1], Fabio DEORSOLA[1], Nikolaos DIMITRATOS[2], Stefania ALBONETTI[2], Fabrizio CAVANI[2], Debora FINO[1], Marco PIUMETTI[*1]

[1]*Polytechnic of Turin, Department of Applied Science and Technology, Corso Duca Degli Abruzzi, 24, 10129, Turin, Italy*

[2] *Alma Mater Studiorum - Bologna University, Department of Industrial Chemistry "Toso Montanari", Via P. Gobetti, 85, 40129, Bologna, Italy*

* marco.piumetti@polito.it

Significance and Relevance

Removing pollutants in confined spaces is essential for improving air quality and well-being. This study investigated gold-functionalized manganese oxides with different crystalline phases to oxidize CO and VOC at low temperatures. The results revealed that gold nanoparticles (AuNPs) enhanced catalytic activity toward all the molecules. Moreover, a relationship between nanoparticle size and catalytic performance was determined, identifying a "critical radius" below which the catalytic efficiency increased substantially and highlighting the importance of optimizing AuNPs for pollutant abatement.

Preferred and 2nd choice for the topic: Air cleaning and combustion; 2nd: Automotive and stationary emission control

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

In recent decades, air purification has gained significant attention, particularly regarding indoor pollution, which can be more hazardous than outdoor pollution. Among the main atmospheric pollutants, Volatile Organic Compounds (VOCs), commonly found in paints and household products, are the most common ones[1]. A promising technology for removing these pollutants is catalytic oxidation at low temperatures. In this context, manganese oxides have proven to be effective catalysts for CO and VOC oxidation due to their activity, durability, and low cost[2]. Different crystalline phases of manganese oxides (such as MnO_2 and Mn_2O_3) exhibit varying catalytic properties, influenced by their redox behavior and structural defects, thus making them effective in oxidizing pollutants like CO, ethylene, and propylene at moderate temperatures[3]. Introducing AuNPs on the surface of these catalysts could further enhance their catalytic activity, improving catalytic performance at even lower temperatures. This approach holds great promise for improving indoor air quality to ensure the health and well-being of people in confined environments.

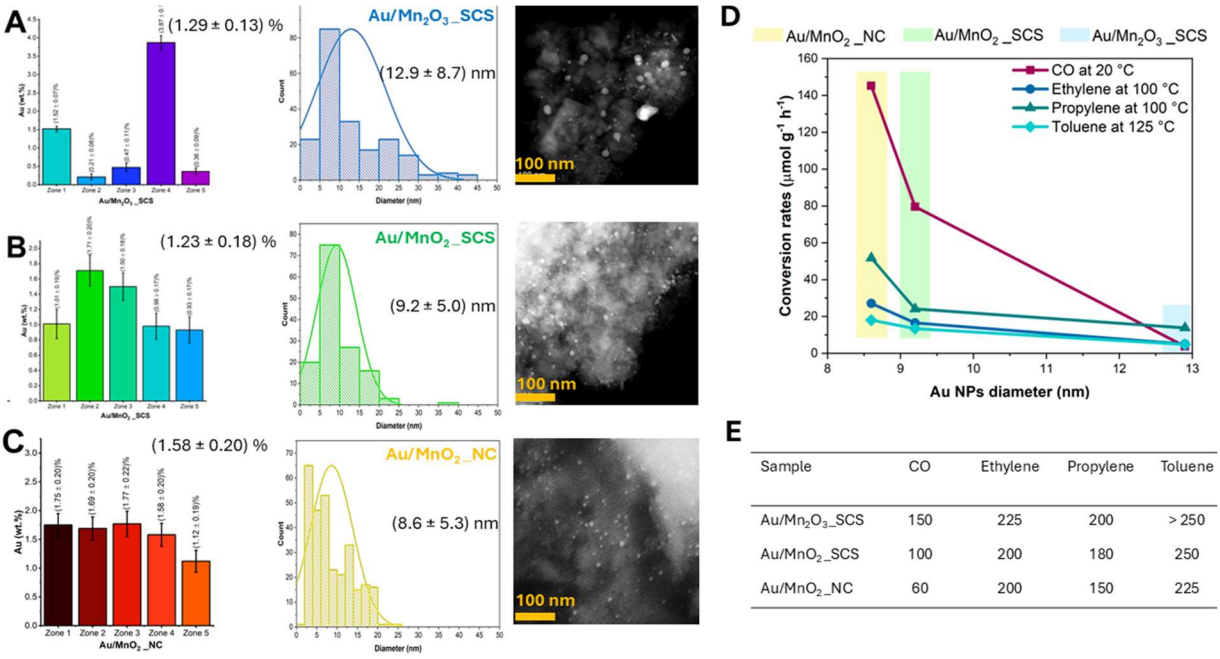
Materials and Methods

Manganese oxides with two different crystalline structures (MnO_2 and Mn_2O_3) were synthesized through the Solution Combustion Synthesis and Nanocasting methods, by following the procedures reported in our previous work[3]. Gold nanoparticles (1 wt.%) were deposited through a sol-immobilization method with the aim of enhancing the catalytic performance at low temperatures. These materials were extensively characterized by different physicochemical techniques, i.e., N_2-physisorption at -196 °C, XRD, XPS, H_2-TPR, O_2-TPD, and STEM-EDX analyses. The catalytic activity was investigated by simulating a real polluted atmosphere containing CO, ethylene propylene, or toluene as target molecules in a concentration of 100 ppm over 50 mg of catalyst. These molecules were chosen since they are common indoor pollutants (e.g., CO) and are difficult to oxidize at low temperatures (e.g., VOCs). Finally, cyclic tests and time on stream (TOS) analyses were carried out on the best-performing catalyst to better investigate the performance and stability of this sample.

Results and Discussion

The catalytic tests revealed highly promising results, particularly in the case of CO conversion. The most striking achievement is its complete conversion at a remarkably low temperature of 60 °C and more than 50 % of conversion at room temperature.

The results obtained in this study highlight the positive impact of AuNPs on the oxidation of VOCs, especially when compared to the unfunctionalized supports. While CO showed a more pronounced response to the presence of AuNPs, with a significant decrease in oxidation temperature of 90 °C for the NC sample compared to the gold-free support (60 °C from 150 °C, respectively), a notable temperature decrease of ~50 °C was also observed for the tested VOCs, highlighting the major potential of AuNPs in promoting oxidation of gaseous pollutants. Another crucial aspect was the effect of the different crystalline structures of MnOx, which influenced the deposition and distribution of NPs. In particular, the MnO_2 phase emerged as the most promising, ensuring optimal NP distribution. The SCS and NC samples showed a more homogeneous NP distribution and a narrower size distribution, with average diameters of 9.2 nm and 8.6 nm, respectively, hinting at a correlation between nanoparticle size and catalytic performance (Figure 1). The best performance was achieved with the higher-surface-area NC sample, indicating that a greater surface area favors better NP distribution and interaction with the reagents. Furthermore, the results led to the identification of a "critical radius", below which catalytic performance significantly increases, particularly for CO, suggesting a pronounced structural sensitivity for this molecule.



Sample	CO	Ethylene	Propylene	Toluene
Au/Mn_2O_3_SCS	150	225	200	> 250
Au/MnO_2_SCS	100	200	180	250
Au/MnO_2_NC	60	200	150	225

Figure 1 AuNPs distribution, average diameter, and STEM images (A-C), the relationship between Au diameter and catalytic performance (D), the temperature at which the conversion is complete (E) for all the pollutants

The ability to achieve full conversion at such low temperatures not only reduces energy consumption but also opens up new possibilities for cleaner technologies. These findings open new perspectives for the optimization of catalysts for air purification, where both the composition and morphology of the catalysts play a decisive role.

References

1. Guo, Y., Appl Catal B, **2021**, 281.
2. Zhou, H., et al., Fuel, **2024**, 366.
3. Grifasi, N., et al., Appl Catal B, **2025**, 362.

Acknowledgements

This study was carried out within the MICS (Made in Italy – Circular and Sustainable) Extended Partnership and received funding from the European Union Next-GenerationEU (Piano Nazionale Di Ripresa E Resilienza (Pnrr) – Missione 4 Componente 2, Investimento 1.3 – D.D. 1551.11-10-2022, PE00000004).

Oxygen Storage Materials in Automotive Catalysts : Composition of CZY

Shota Hamada[1], Daiju Matsumura[2], Shinya Uegaki[1] , Hidetaka Tanabe[1] , Tomohito Nakayama[1], Itsuki Jinjo[1], Seita Kurono[1], Masami Nakamoto[3], Tomohisa Mizuno[4],Takashi Goto[4], Hirohisa Tanaka*[1]

[1]*Kwansei Gakuin University, Graduate School of Science and Technology, Sanda, Hyogo, Japan.*

[2] *Japan Atomic Energy Agency, SPring-8., 1-1-1 Koto Sayo, Sayo, Hyogo, Japan.*

[3]*Daihatsu Motor Co., Ltd., 2-1-1 Momozono, Ikeda, Osaka, Japan.*

[4]*Cataler Corporation, 1905-10 Shimonobe, Iwata, Shizuoka, Japan.*

** e-mail corresponding : hirohisa.tanaka@kwansei.ac.jp*

Significance and Relevance

The optimal composition of ceria-based composite oxides was investigated for oxygen storage capacity (OSC), which is important for automotive catalysts. Weight changes due to oxygen storage capacity were measured using thermogravimetric balance, and valence changes of ceria and other elements were observed at the K-edge of Ce, Zr, and Y using dispersive X-ray absorption fine structure (DXAFS) at SPring-8. Some interesting results were obtained, such as the Ce valence change slowing down when the amount of precious metal was increased. Observations of changes in the weight of the catalyst and changes in the valence of elements make this discovery possible.

Introduction and Motivations

The upcoming Euro 7 regulations will be stricter than ever before, and automakers will need to take on more challenging challenges. In order to comply with these strengthened regulations, automobile manufacturers need to conduct research into catalysts that can meet the strengthened regulations. In this study, we studied what changes occur when the ceria ratio in automobile catalysts is changed, in order to provide a guideline for future catalyst development.

Materials and Methods

A composite oxide with different ceria ratios was prepared as an automobile catalyst with OSC. As a durable product, it was subjected to durability in a rich (CO) and lean (O2) atmosphere as a driving treatment of a car, and the temperature was lowered in a lean atmosphere. In addition, in the initial product, it was treated in a model gas with A/F = 14.4 to stabilize the initial state.

This time, samples with different ceria ratios were prepared. The powder was prepared so that the weight ratio of ceria in the CZY powder composition was 20, 40, and 57%, and precious metals were supported.

The experiment was performed by flowing reducing gas and oxygen alternately five times every 100 seconds to observe the changes caused by releasing and storing oxygen.

Table 1. types of ceria-based complex oxides

Code	Oxide weight ratio			Composition (Atomic ratio)
	CeO_2	ZrO_2	Y_2O_3	
CZY20	20	73	7	$Ce_{0.15}Zr_{0.77}Y_{0.08}O_{2-\delta}$
CZY40	40	55	5	$Ce_{0.32}Zr_{0.62}Y_{0.06}O_{2-\delta}$
CZY57	57	39	4	$Ce_{0.49}Zr_{0.46}Y_{0.05}O_{2-\delta}$

Results and Discussion

To observe the weight change of the catalyst and the local structural change of cerium due to H_2 or CO reduction and O_2 oxidation, we performed experiments to observe the mass change using a thermogravimetric balance and analysis by time-resolved dispersive X-ray absorption fine structure (DXAFS) near the Ce *K*-edge at the BL14B1 beamline of SPring-8[3][4].

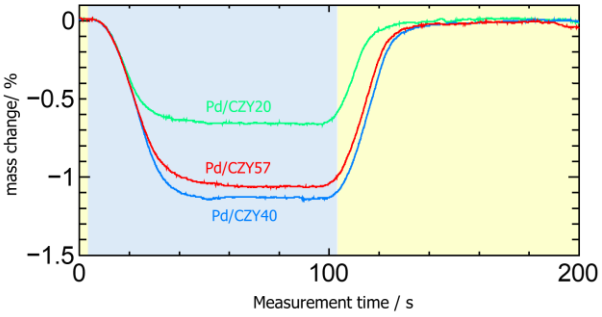


Figure 1. Comparison of ceria ratios using a thermogravimetric device

First, Pd/CZY20, Pd/CZY40, and Pd/CZY57, which have different ceria ratios, were reduced with hydrogen and oxidized with oxygen, and the mass change was observed using a thermogravimetry

balance (Figure 1). When reduced with hydrogen, oxygen is released and the mass decreases, and when oxidized with oxygen, oxygen is absorbed and the mass increases. Figure 1 shows the percentage of mass that is reduced when reduced, based on the oxidized state.

In this study, the mass change was greatest for Pd/CZY40, where the ceria mass ratio was 40, followed by Pd/CZY57 and Pd/CZY20. This suggests that the difference in ceria ratio has a significant effect on the amount of oxygen stored.

Next, using the same sample, we observed CO reduction and O_2 oxidation in an experiment using time-resolved dispersive X-ray absorption fine structure (DXAFS) near the Ce K-edge at the BL14B1 of SPring-8 (Figure 2).

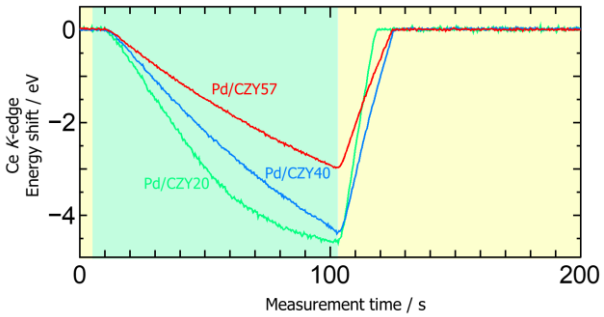


Figure 2. Comparison of ceria ratios by DXAFS

Unlike the thermogravimetric balance used earlier, we found that the lower the cerium ratio, the faster the reaction. What is noteworthy here is that as the cerium ratio decreases, the zirconium-yttrium ratio increases. This shows that as the zirconia ratio increases, the reduction and oxidation rates of ceria become faster[5]. As such, the OSC and reaction rate change depending on the ratio of cerium to zirconium, so when designing a catalyst or sensor, it is necessary to take into account the balance between the required OSC and reaction rate.

References

1. H. Tanaka, M. Yamamoto, 1996, Improvement in oxygen storage capacity, 231-238.
2. K. Yamada, H. Tanaka, M. Yamamoto, 1997, Oxygen storage capacity on cerium oxide-precious metal system, 1-8.
3. D. Matsumura, Y. Nishihata, J. Mizuki, et al. 2010, Dynamic structural change in Pd-perovskite automotive catalyst studied by time-resolved dispersive x-ray absorption fine structure,
4. Yasutaka Nagai, Takashi Yamamoto, Tsunehiro Tanaka, Satohiro Yoshida, Takamasa Nonaka, Tokuhiko Okamoto, Akihiko Suda, Masahiro Sugiura, 2002, X-ray absorption fine structure analysis of local structure of CeO_2-ZrO_2 mixed oxides with the same composition ratio (Ce/Zr=1), 225-234.
5. Shawn Rood, Salvador Eslava , Alexis Manigrasso, Chris Bannister, 2019, Recent advances in gasoline three-way catalyst formulation: A review, 936-949.

Acknowledgements

The synchrotron radiation experiments were performed at SPring-8 QST beamline BL14B1 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal Nos. 2023B3618 and 2024A3618). A part of this work was supported by the Advanced Research Infrastructure for Materials and Nanotechnology in Japan (ARIM Japan) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan (Grant Nos. JPMXP1223AE0021 and JPMXP1224AE0003) and the Shared-Use Program of JAEA Facilities (Proposal Nos. 2023B-E04 and 2024A-E06).

Optimizing Iron-Containing Beta Zeolites: Influence of Synthesis Methods on Methane Oxidation Performance

Anne NIEDERDRÄNK[*,1,2], Merle BLUM[1,2], Olaf HINRICHSEN[1,2]
[1] *Technical University of Munich, School of Natural Sciences, Lichtenbergstr. 4, 85748 Garching, Germany.*
[2] *Technical University of Munich, Catalysis Research Center, Ernst-Otto-Fischer-Str. 1, 85748 Garching, Germany.*
** anne.niederdraenk@tum.de*

Significance and Relevance

This study focuses on developing cost-effective, yet highly active and stable, non-precious catalysts to reduce methane emissions from marine engines, aiming to reduce greenhouse gases in the maritime sector to promote environmentally friendly maritime technologies. It also indicates a potential of iron-containing beta zeolites, already widely used for NO_x reduction by SCR, as a dual-purpose application for mitigating various emissions.

Preferred and 2nd choice for the topic: Automotive and stationary emission control, Air cleaning and combustion
Preferred presentation: Poster

Introduction and Motivations

Dual fuel and gas-powered marine engines offer significant potential for reducing greenhouse gas (GHG) emissions in the maritime sector, such as CO_2, NO_x and particulate matter, in order to meet the growing demand for improved environmental and climate protection.[1] However, a key challenge remains the emission of unburned CH_4. Since CH_4 is significantly more potent as a GHG than CO_2, further oxidation to CO_2 is required. Until now, platinum group metal catalysts have typically been used for total oxidation of CH_4. Due to their high costs and low stability against water and sulfur, novel non-precious catalysts with high activities and stabilities need to be developed. Cheap and non-toxic iron-containing beta zeolites have already been proven for selective catalytic reduction (SCR) of NO_x in exhaust catalysis,[2] and are thus promising candidates for coupling SCR with methane oxidation. This study explores the synthesis and successful application of iron beta zeolites in the complete oxidation of methane.

Materials and Methods

The investigated catalysts were prepared by introducing iron nitrate into commercial beta zeolites through methods based on wetness impregnation, solid ion exchange and liquid ion exchange. As reference, the parent pure beta zeolite without iron was used. All materials were subsequently calcined at 550 °C. Structural characterization included amongst others X-ray powder diffraction (XRD), N_2 physisorption analysis, atomic absorption spectroscopy (AAS), transmission electron microscopy (TEM), infrared spectroscopy (IR) and temperature programmed desorption (TPD) measurements of NO. Activity measurements were conducted under specific CH_4 and O_2 concentrations at temperatures ranging from 400 – 650 °C and pressures up to 6 bar.

Results and Discussion

Detailed characterization of the synthesized catalysts revealed that the method of iron incorporation into the zeolite influences the catalyst acidity and both the distribution and the type of iron species present. Solid ion exchange, for instance, led to the formation of a hematite phase. In contrast, no crystalline iron phase was detected in catalysts prepared by the other methods, suggesting a fine dispersion or an incorporation of iron into the zeolite framework. The results of the activity measurements are shown in Figure 1 as the specific methane conversion rate, relative to the iron loading of the catalyst. The measurements clearly indicate an impact of iron species on the activity for complete methane oxidation. Here, the catalyst from solid ion exchange (SIE) with a hematite phase

revealed the lowest activity. The catalyst from wetness impregnation (IWI) showed a higher iron dispersion and thus an enhanced activity towards methane oxidation. In contrast, liquid ion exchange (LIE) resulted in catalysts with superior activity, possibly due to better integration of iron into the zeolite framework.

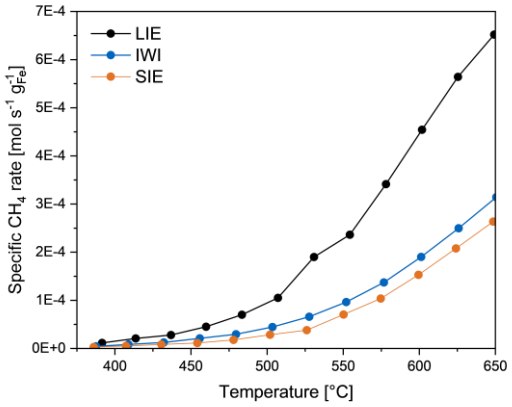


Figure 1 Catalytic activity of the catalysts depending on the temperature.

The study concludes that the method of iron incorporation critically influences catalyst properties and performance, with liquid ion exchange yielding the most active catalysts for methane oxidation due to superior iron integration into the zeolite framework.

References

1. W. Peng, J. Yang, J. Corbin, U. Trivanovic, P. Lobo, P. Kirchen, S. Rogak, S. Gagné, J.W. Miller, D. Cocker, *Environ. Pollut.* **2020**, *266*, 115404.
2. A.M. Frey, S. Mert, J. Due-Hansen, R. Fehrmann, C.H. Christensen, *Catal. Letters* **2009**, 130, 1-8.

Acknowledgements

The authors acknowledge the support by the German Federal Ministry for Economic Affairs and Climate Action, grant number 03SX535B.

NH_3 decomposition of Al_2O_3 bead surface modified Ru catalysts to produce carbon-free hydrogen

[1]Younghwan Im, [1]Sung Min Kwon, [1]Minsik Kim, [1]Youngmin Kim, [1]Ho-Jeong Chae[*,]
[1]Hydrogen & C1 Gas Research Center, Korea Research Institute of Chemical Technology, 141 Gajeong-ro, Yuseong-gu, Daejeon, Republic of Korea.

** hjchae@krict.re.kr*

Significance and Relevance

Developing highly active catalysts with low noble metal content is essential for reducing catalyst costs and making them commercially viable. We have developed a coating method on bead supports to fabricate NH_3 decomposition catalysts with reduced Ru content, providing a pathway to more economical catalysts for industrial applications.

Preferred and 2nd choice for the topic: "Ammonia decomposition and Carbon-free hydrogen production"
Preferred presentation: "Poster"

Introduction and Motivations

Ammonia is one of the promising hydrogen carriers because of high hydrogen content (17.7 wt.% H_2), carbon-free conversion to hydrogen and nitrogen, and mild liquefaction condition (- 33.4 °C at 1 atm, or 8.5 atm at 20 °C) [1]. At the end of the NH_3 transport, the NH_3 gas should be converted to H_2 and N_2 using NH_3 decomposition catalyst, of which should have outstanding catalytic performance and low cost. Therefore, we developed the Ru based catalysts, which used surface-modified Al_2O_3 bead support to enhance catalytic performance and reduce Ru content.

Results and Discussion

The purpose of the $Ru/LaCeO_x/Al_2O_3$ bead catalyst synthesized by our method is to increase in catalytic activity for NH_3 decomposition while decreasing Ru content, simultaneously, our method was also concerned for ease to be commercialized.

Fig. 1 shows the NH_3 conversion of the commercial (pellet and bead coating catalysts) and synthesized Ru based catalysts at 3,000 mL $g_{cat.}^{-1}$ h^{-1} under 100 % NH_3. The $Ru/LaCeO_x/Al_2O_3$ catalyst, which we have made with our method, exhibited better NH_3 decomposition performance than the other commercial Ru based catalysts (A – C co.) and Ru catalyst, which $LaCeO_x$ layer was formed by normal impregnation method (Ru cat. normal method).

In addition, the $Cs\text{-}Ru/LaCeOx/Al_2O_3$ bead catalyst had the promoted catalytic activity more than the no Cs-promoted $Ru/LaCeO_x/Al_2O_3$ bead catalyst.

Fig. 2 shows the elemental mapping image of the $Ru/LaCeO_x/Al_2O_3$ bead (cross-section) and elemental composition analyzed by ICP-OES. In this catalyst, the main metal species including Ru and promoting support materials, La and Ce oxide were evenly formed onto the thin sub-surface of Al_2O_3 bead, indicating that expensive material, such as Ru, La, and Ce were dispersed on the bead catalyst's surface and could be saved for the $Ru/LaCeO_x/Al_2O_3$ bead catalyst. Especially, the Ru content was 0.66 wt%, which is very low Ru content compared to the other commercial catalysts. It indicates that our shaped catalyst developed in this work, the $Ru/LaCeOx/Al_2O_3$ bead catalyst, has excellent catalytic activity although Ru and the other expensive element, such as La and Ce contents were very low.

Conclusively, we have developed the low cost and high active Ru bead catalyst for NH_3 decomposition, and it was better than the other commercialized Ru based pellet and bead coating catalysts even it had low Ru content.

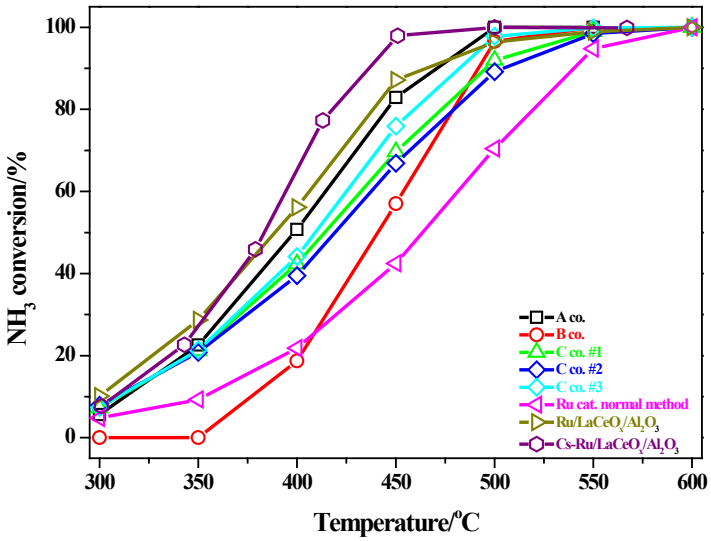


Figure 1. NH_3 conversion of Ru based catalysts; commercial and synthesized $Ru/LaCeO_x/Al_2O_3$ bead catalysts with normal impregnation (Ru cat. normal method) and our methods ($Ru/LaCeO_x/Al_2O_3$ and $Cs\text{-}Ru/LaCeO_x/Al_2O_3$) (SV: 100 % NH_3 3000 mL $g_{cat.}^{-1}$ h^{-1})

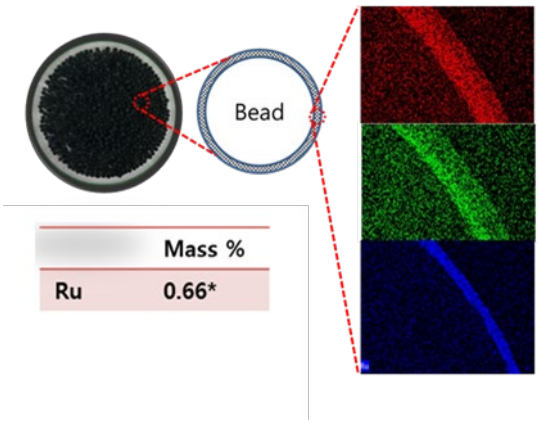


Figure 2. Elemental mapping image (cross-section) and Ru content of $Ru/LaCeO_x/Al_2O_3$ bead catalyst analyzed by SEM-EDS and ICP-OES of $Ru/LaCeO_x/Al_2O_3$ bead catalyst (Red: Ce, Green: La, Blue: Ru)

References

1. S. Sun, *Renewable and Sustainable Energy Reviews, **2022**,* 169, *112918*.

Acknowledgements

This work was supported by the core KRICT project (KK2411-30) from the Korea Research Institute of Chemical Technology (KRICT) and by the National Research Council of Science & Technology(NST) grant by the Korea government (MSIT) (No. GTL24051-200).

Ti-MCM-22 catalysts for selective oxidation of organic sulphides by H_2O_2

Aleksandra Jankowska*[1], Wiktoria Dubiel[1], Andrzej Kowalczyk[1], Małgorzata Rutkowska[1], Lucjan Chmielarz[1]
[1]*Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, 30-387, Kraków, Poland.*
** aleksandra1.jankowska@uj.edu.pl*

Significance and Relevance

In recent years, environmental regulations on sulphur reduction in petroleum processing have become stricter. The widely used hydrodesulphurization (HDS) process demands high temperatures, pressure, and catalysts, increasing energy consumption and costs.[1] Additionally, handling sulphur-containing waste remains a challenge. Oxidative desulphurization (ODS) is emerging as a promising alternative, aiding in zero-sulphur fuel production and waste removal. This process also plays a crucial role in pharmaceuticals, as the oxidation of aromatic compounds like diphenyl sulphide (Ph_2S) produces key reagents for drug synthesis. While strong oxidants such as $KMnO_4$ are effective, they generate hazardous waste.[2] Hydrogen peroxide (H_2O_2) offers a greener alternative but requires catalytic conditions for efficiency. Ti-based catalysts have shown potential, though debate continues over the precise active sites in selective oxidation.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion or Sustainable and clean energy production and transport.
Preferred presentation: Poster

Introduction and Motivations

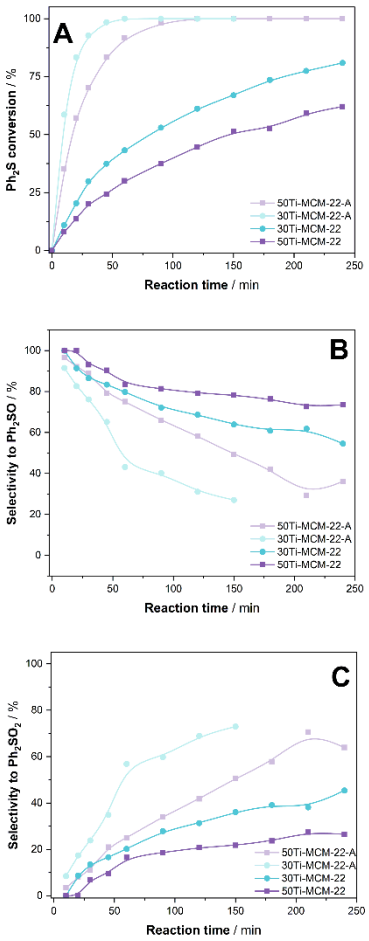
The MWW-structured zeolite, with MCM-22 as its key representative, is a notable example of a layered zeolite, obtained by calcining its precursor, MCM-22(P).[3] MCM-22 is widely utilized in hydrocarbon conversion and holds potential for various catalytic applications. Conventional zeolites like MCM-22 are crystalline aluminosilicates, but incorporating other metal cations into MWW structures enhances their catalytic properties. Specifically, introducing heteroatoms such as titanium into the zeolite framework expands possibilities for tailored applications in zeolite synthesis. Titanium-containing porous silica systems were found to be promising catalysts for the application in selective oxidation of organic sulphides by hydrogen peroxide.[2] Hence, the main goal of the presented studies was to determine the efficiency of the selective catalytic oxidation of Ph_2S by H_2O_2 in the presence of Ti-MCM-22 zeolite.

Materials and Methods

In this study, a modern heteroatom layered Ti-MCM-22(P) zeolite was synthesized by a one-pot method with two different Si/Ti molar ratios (30 and 50). The resulting layered precursors were then treated with nitric acid (HNO_3) to remove extra-lattice titanium species, ensuring that only framework titanium cations remained in the final material. This approach differed from the untreated precursor, which underwent calcination without prior acid treatment. The primary objective was to investigate how titanium aggregation affects the efficiency of selective catalytic oxidation of organic sulphides using H_2O_2. The synthesized zeolites were analyzed for their chemical composition (ICP-OES), structure (XRD, UV-vis DRS), textural properties (low-temperature N_2 sorption), and surface acidity (NH_3-TPD).

Results and Discussion

The study concluded that the synthesized Ti-MWW derivatives exhibited a high conversion rate and excellent selectivity toward sulfone (Figure 1). The variations in catalytic activity between the untreated zeolites (30Ti-MCM-22 and 50Ti-MCM-22) and those subjected to acid treatment during synthesis (30Ti-MCM-22-A and 50Ti-MCM-22-A) were attributed to differences in the form and aggregation of titanium within the materials.



After 240 minutes of reaction, Ph_2S conversion was achieved at the level of 62 and 81%, respectively, for samples with increasing titanium content in the material – 50Ti-MCM-22 and 30Ti-MCM-22 (Figure 1 A). The main reaction product for both samples is Ph_2SO (Figure 1 B), with selectivity at the level of 73% and 56% for 50Ti-MCM-22 and 30Ti-MCM-22, respectively. It can be observed that in the case when the complete conversion of the Ph2S substrate was not achieved, the oxidation of Ph_2SO to Ph_2SO_2 is less efficient (Figure 1 C). Samples refluxed with acid, despite having lower titanium content due to Ti extraction, exhibit better catalytic properties. Therefore, it can be stated that the key role in this case is played by monomeric, tetrahedrally coordinated titanium cations. In the case of acid-treated zeolites, their presence was confirmed by the analysis of UV-vis DRS (Figure 2). Under conditions of the HNO_3 modification at the synthesis stage, extra-lattice forms of titanium were extracted from the framework and a structure was obtained in which titanium was introduced mainly in the form of monomeric, tetrahedrally coordinated cations. For these materials, the absorption maximum occurs at about 230 nm, indicating the presence of mainly monomeric, tetrahedrally coordinated titanium cations.[4] In the spectra recorded for materials that were not subjected to such modification, the presence of more polymerized forms of titanium was identified. In those cases, absorption maxima occur at about 275 nm. They are related to the presence of extra-lattice, octahedrally coordinated titanium cations. The shoulder above 320 nm can be attributed to the presence of small amounts of TiO_2.[4]

Figure 1 Catalytic test results for Ti-MWW derivatives; **A**: Ph_2S conversion, **B**: selectivity to Ph_2SO, **C**: selectivity to Ph_2SO_2.

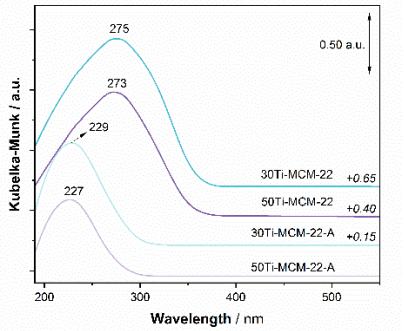


Figure 2 UV-vis DR spectra recorded for the Ti-MWW derivatives.

References

1. M. Muñoz, M. Greber, K. Ben Tayeb, C. Lamonier, C. I. Cabello, G. P. Romanelli; *Green Process. Synth*. **2023**, 12, 20230026.
2. W. Dubiel, A. Kowalczyk, A. Jankowska, M. Michalik, W. Mozgawa, M. Kobielusz, W. Macyk, L. Chmielarz, *Green Process. Synth.* **2023**; 12, 20230052.
3. J. Čejka, B. Wichterlová, *Catal. Rev*. **2002**, 44, 375–421.
4. P. Wu, T. Tatsumi, T. Komatsu, T. Yashima, *J. Phys. Chem. B* **2001**, 105(15), 2897-2905.

Acknowledgements

The research has been supported by a grant from the Faculty of Chemistry under the Strategic Programme Excellence Initiative at Jagiellonian University.

Defect-rich Mo/MoO_2 catalyst for efficient peroxymonosulfate activation and refractory pollutants degradation

Hongjun FANG, Hui GUO, Xinzhen FENG, Weijie JI*
Key Laboratory of Mesoscopic Chemistry, MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China
**e-mail: jiwj@nju.edu.cn*

Significance and Relevance

A Mo/MoO_2 catalyst fabricated *via* electro-explosive method comprises enriched oxygen vacancies, capable of rapid redox cycles among $Mo^{4+}/Mo^{5+}/Mo^{6+}$ and accelerates electron transfer kinetics, more conductive to catalytic degradation of acid orange (AO7). A degradation of AO7 with a rate constant of 1.108 min^{-1} was achieved on the Mo/MoO_2-10h/PMS system. Relative significance of AOSs in the current system was identified as $^1O_2 > {}^{\bullet}O_2^- > {}^{\bullet}OH > SO_4^{\bullet}$. The detailed AO7 degradation pathways have been proposed in terms of the LC/MS analysis. This system also exhibited high performance for removal of a variety of pollutants including antibiotics and organic dyes.

Introduction and Motivations

Acid orange 7 (AO7) is frequently detected in textile wastewater and poses an ongoing impact on aquatic ecosystems because of its high ecotoxicity and water solubility.[1,2] For effective AO7 removal, advanced oxidation processes (AOPs) have been taken into consideration. Among these AOPs, the sulfate radical-based AOP using peroxymonsulfte (PMS) as oxidant has the merits of stronger oxidation capacity, wider pH adaptability, and higher stability, thus more suitable for refractory pollutants removal (Yang et al., 2021a and 2022b). At present, various activation methods are applied to activate PMS, yielding active oxygen species for pollutants degradation. However, development of high-performance catalyst (high activity/durability) for PMS activation is still challenging.

Materials and Methods

The electro-synthesis of Mo and Mo/MoO_2 catalysts was operated on a commercially available apparatus (Thor Series Nano Metal Machine) with the Mo wire as raw material. This electric-explosion method is environmentally friendly and free of additional chemical reagents. The fresh sample was subjected to an oxidation exposure in air for different time (5 h, 10 h, and 20 h), and denoted as Mo/MoO_2-5 h, Mo/MoO_2-10 h, and Mo/MoO_2-20 h, respectively. Meanwhile, the reference sample MoO_2-H with deficient Vo was synthesized by hydrothermal method for comparison. The catalytic activity of each sample was evaluated by degradation of AO7 with PMS oxidant. The catalysts were characterized by various techniques and the DFT simulation was also performed to better understand the catalyst properties and the reaction details.

Results and Discussion

Defect engineering has been proven to alter the electron mobility of catalyst by generating high content of defects (i.e., Vo), thus favorable for electron transfer and providing more active sites for catalytic reactions. Integration of Mo^0 and Vo into MoO_2 could significantly improve the activity of the resulting material. Notably, the traditional catalyst synthesis usually involved the use of various chemical reagents, which also poses additional negative impact on the environment. Therefore, a facile synthesis route without additional chemical input and easy to scale-up is highly desirable for practical application. This work reported a convenient electric explosion route to obtain the Vo-rich Mo/MoO_2 system using the Mo wire as raw source without employing any additional chemicals. Evidently, the Mo site of different oxidation states contributed to chemical activation of PMS, while the Vo favored the activation of PMS and the generation of non-radical $^1O_2$ species. As a result, the Mo/MoO_2-10 h/PMS system delivered a complete removal of acid orange 7 (AO7) within 4 min, significantly exceeding the activity of Mo/PMS (16%), MoO_2-H/PMS (25%), and most of other PMS-based systems. Theoretical calculations revealed that the PMS dissociation is not a rate-determining step in the

involved system, while the activation efficiency of catalyst is largely related to the difference of its binding ability to PMS. Expectedly, the Vo-rich Mo/MoO_2 owned a stronger adsorption capacity of PMS and rapider electron transfer kinetics compared to that of Vo-deficient MoO_2, thereby accounting for an enhanced catalytic activity for the PMS-AOP. Quenching experiments and EPR analysis suggested that the $^1O_2$ species was the dominated one for AO7 removal. Toxicity prediction analysis of the original, the intermediates, and the final products indicated that the degradation intermediates were less toxic to the environment. Moreover, the current system showed high potential for removal of different pollutants such as CIP, TC, RhB, and MB.

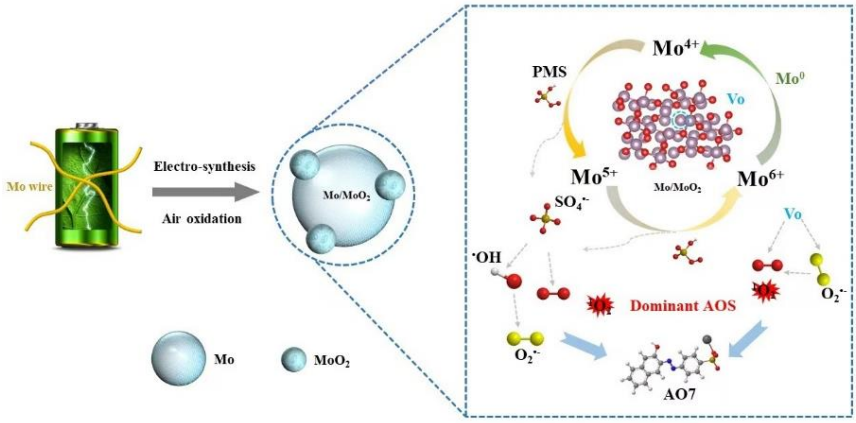


Figure 1 Schematical illustration of electro-explosive route to synthesize the oxygen vacancy enriched Mo/MoO_2 catalyst, the involved PMS activation, and the critical AOS of $^1O_2$ formation.

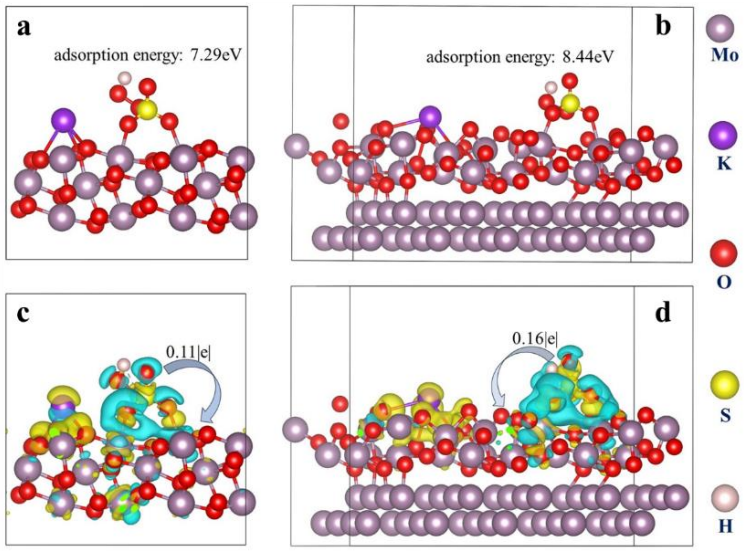


Figure 2. The calculated adsorption energy of (a) MoO_2 (-111) surface and (b) the Mo (110)/MoO_2 (-111) interface; the charge density difference of (c) MoO_2 (-111) surface and (d) the Mo (110)/MoO_2 (-111) interface.

References

1. M. Li, Z. L. Li, X. L. Yu, Y. L. Wu, L. G. Li, N. Wang, S. W. Chen, *Chem. Eng. J.* **2022**, *431*, 13333.
2. J. Zhang, X. Shao, C. Shi, S. Yang, *Chem. Eng. J.* **2013**, *232*, 259-265..
3. L. Yang, H. Chen, F. F. Jia, W. J. Peng, X. Tian, L. Xia, X. Y. Wu, S. X. Song, *ACS Appl. Mater. Interfaces* **2021**, *13*, 14342-14354.

Acknowledgements

We greatly appreciate the financial support from NSFC (22072063) and MSTC (2020YFE0100100).

Process Informatics of High-Entropy Alloy for Automotive Catalysis

Azusa Kamiyama[1], Kohei Kusada[2,3], Hiromasa Kaneko[4], Megumi Mukoyoshi[2],
Masafumi Sakota[1], Hiroto Tsuchiya[1], Atsushi Furukawa[1], Hiroshi Kitagawa[2] and Hitoshi Mikami[1*]
[1]*Honda R&D Co., Ltd., Innovative Research Excellence, 4630 Shimotakanezawa, Haga-machi, Haga-gun, Tochigi, Japan.*
[2]*Kyoto University, Division of Chemistry, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto, Japan*
[2]*Kyoto University, The Hakubi Center for Advanced Research, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto, Japan*
[4]*Meiji University, Department of Applied Chemistry, 1-1-1 Higashi-Mita, Tama-ku, Kawasaki, Kanagawa, Japan*
**hitoshi_mikami@jp.honda*

Significance and Relevance

We successfully developed a material screening method and explored High-Entropy Alloy (HEA) catalysts which show higher activity for exhausted gas purification than Pd mono-metal catalyst from huge search space. This method is based on high-throughput screening and direct inverse analysis and optimizes the elemental species, composition, and synthesis conditions for the catalyst with high catalytic activity and durability. By using this method, the search efficiency was increased by 200 times compared to conventional methods.

Preferred and 2nd choice for the topic: Automotive and stationary emission control and Air cleaning and combustion
Preferred presentation: Poster

Introduction and Motivations

Automotive catalysts are essential for creating eco-friendly automobiles. Much effort has been devoted to enhancing their performance and reducing their costs by selecting metals and support materials. Recently, HEA nanoparticles have attracted much attention due to unique properties which do not appear in the bulk.[1] Therefore, we expected that HEA can dramatically improve the performance of automotive catalysts. However, it is challenging to search HEA catalysts by using traditional search methods which rely on the researcher's experience, intuition, and good luck, due to an enormous number of combinations and compositions of elemental species, and synthesis conditions. In this study, we conducted process informatics to obtain HEA catalysts with high catalytic activity for exhaust gas purification catalysts.

Results and Discussion

The process informatics platform was developed as shown in Figure 1(a). The catalysts were synthesized by the automatic flow reactor based on a homemade flow reactor[3], and their activities were evaluated by a high-throughput screening (HTS) which can perform not only evaluation but also durability testing and pre-treatment for reduction. Results of evaluation were used for direct inverse analysis which can directly predict x values by putting target y values into the GMR model to obtain some recipes with a high possibility to achieve the target of activity performance.[2] Approximately 80 samples were synthesized and analyzed each week, totaling approximately 1,500 samples evaluated over one year. Figure 1(b) shows the performance results of predicted HEA catalysts with fixed elemental species and varying synthesis conditions. These results show that their catalytic performance varies with different synthesis conditions, suggesting the importance of investigating not only materials but also the synthesis conditions. Detailed results of our study and future plans toward the product development will be discussed in the presentation.

(a) (b)

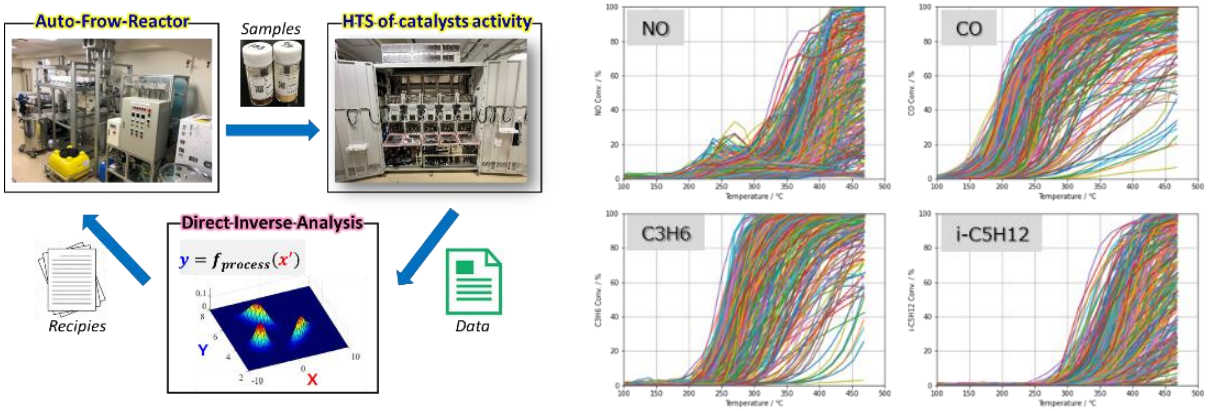


Figure 1 (a) Process informatics platform and (b) results of high-throughput screening of HEA with fixed the elemental species and different synthesis conditions.

References

1. K. Kusada etal., Angew. Chem. Int. Ed., **2022**, 61, e202209616.
2. H. Kaneko, Chemom. *Intell. Lab. Syst.*, **2021**, 208, 104226.
3. K. Kusada etal., *J. Phys. Chem. C*, **2021**, 125, 458.

Acknowledgements

The authors are grateful thank to Prof. M. Koyama's group at Shinshu University for their kind advice on computational chemistry, to Prof. Masaaki Haneda at Nagoya Institute of Technology for infrared spectroscopy, and to Prof. Murakami's group at Kyushu University for TEM measurements.

Complete oxidation of methane over Pd/zeolite catalysts for lowering the reaction temperature

Min Sik KIM[1], Younghwan IM[1], Youngmin KIM[1], Yeon Jin LEE[1], You-Jin LEE[1], Ho-Jeong CHAE[*,1]
[1]*Korea research institute of chemical technology, Hydrogen & C1 gas research center, 141 Gajeong-ro Yuseong-gu, Daejeon, South Korea.*
** hjchae@krict.re.kr*

Significance and Relevance

Zeolite supported Pd catalysts were tested for complete methane oxidation, achieving a high methane conversion of over 90% at 370°C. In addition, the catalyst demonstrated stable methane conversion performance over 100 hours of continuous operation, demonstrating its durability and effectiveness in long-term applications.

Preferred for the topic: "Automotive and stationary emission control"
Preferred presentation: "Poster"

Introduction and Motivations

In response to global warming, there is a shift towards the use of natural gas as a cleaner energy source for ships.[1] However, 'methane slip' is a major challenge and a significant environmental concern due to methane's high global warming potential.[2] Currently, there is no promising solution for methane slip in marine engines. Generally, palladium-based catalysts, such as Pd/Al_2O_3, are widely used for methane oxidation, but they face challenges under methane slip conditions due to the presence of water, which does not completely deactivate the catalyst but reduces its activity by covering active sites.[3] In this study, we prepared palladium catalysts supported on several zeolites, which have morphology properties to overcome water coverage.

Results and Discussion

Pd/zeolite catalysts were prepared by varying the parameters at the preparation step. The type of zeolite, Pd precursor, solvent and the Pd content were the main parameters for the catalyst synthesis. Among them, the best performing catalyst achieved about 95% methane conversion with containing about 7% H_2O at 370 °C. (**Figure 1**)

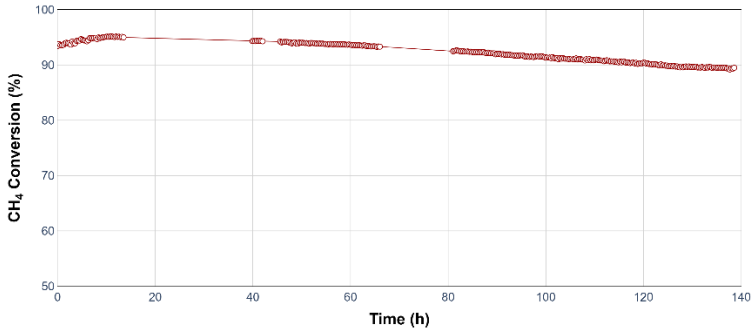


Figure 1. Complete oxidation of methane over Pd/zeolite catalyst at 370 °C for more than 100 hours, Reaction condition: 0.5% CH_4, 5% O_2, 7.1% H_2O in Ar balance, 120,000 $mL \cdot g_{cat}^{-1} \cdot h^{-1}$ GHSV

References

1. S. Ushakov, D. Stenersen, P. Einang, *Journal of Marine Science and Technology* **2019**, *24*, 1308.
2. R. Mortensen, H. Noack, K. Pedersen, S. Mossin, J. Mielby, *ChemCatChem* **2022**, *16*, e202101924.
3. P. Losch, W. Huang, O. Vozniuk, E. Goodman, W. Schmidt, M. Cargnello, *ACS Catalysis* **2019**, *6*, 4742.

Acknowledgements

This work was supported by the Korea Planning & Evaluation Institute of Industrial Technology (KEIT) (No. 20024949) from the Ministry of Trade, Industry and Energy (MOTIE) of the Republic of Korea and by the core KRICT project (KK2411-30) from the Korea Research Institute of Chemical Technology (KRICT).

Sustainable conversion of biomass waste to levulinic acid and hydrochar via wet torrefaction with H-Beta zeolite catalyst

Andrii Kostyniuk[1]*, Blaž Likozar[1]
[1]*National Institute of Chemistry, Department of Catalysis and Chemical Reaction Engineering, Hajdrihova 19, Ljubljana, 1001, Slovenia*
**andrii.kostyniuk@ki.si*

Significance and Relevance

Wet torrefaction (WT) is an effective pretreatment method of biomass waste for producing high-quality hydrochar and valuable liquid products. This study delves into how acid catalyst and reaction conditions in WT impact the resulting hydrochar's surface characteristics and elemental composition, as well as the distribution of liquid products. The focus is on utilizing wood cellulose pulp residue (WCPR) as the feedstock with H-Beta zeolite catalyst in a nitrogen-rich environment [1].

Introduction and Motivations

Biomass, known for its near carbon-neutral properties and abundant availability in nature, offers the potential to substantially decrease fossil fuel consumption and environmental pollution, particularly in reducing greenhouse gas emissions [2]. Cellulose, hemicelluloses, and lignin form the principal constituents of lignocellulosic biomass, accompanied by minimal amounts of organic extractives and inorganic minerals. Wood cellulose pulp residue (WCPR) is the leftover material that remains after extracting cellulose fibers from wood, a process achieved through physical, chemical, or biological methods, commonly used in several industrial sectors, particularly in the paper and pulp industry [3]. This residual material consists of various wood components that do not get transformed into cellulose fibers during the pulping process. Recent data provided by Statista reveals a consistent and robust performance in the global pulp industry, with production consistently exceeding 180 million metric tons on an annual basis for the past decade. In 2022, the global production of wood pulp experienced a notable surge, reaching over 195.8 million metric tons.

Materials and Methods

The H-Beta zeolite catalyst, featuring a SiO_2/Al_2O_3 ratio of 28, was procured from the commercial supplier Tosoh Corporation. This zeolite catalyst underwent a calcination process at 550 ◦C (10 ◦C/min) in the air for 6 h to remove impurities before being used in the study. All chemical reagents, calibration standards, and gases were commercially sourced and used without the need for further purification. Wet torrefaction of wood cellulose pulp residue (WT WCPR) reactions were conducted in autoclave steel batch reactors (6 Parr 5000 Multiple Reactor System), each with a capacity of 75 mL and equipped with online pressure and temperature control regulators [4].

Results and Discussion

The WT process involves a temperature range of 180–260 ◦C, and reaction durations spanning 15–60 min. The findings reveal that WT conditions, including the catalyst for WCPR, significantly influence the hydrochar's properties and liquid product distribution. With increasing temperature and reaction time, the hydrochar experiences changes, including increased carbon content and reduced oxygen content. The study identifies 260 ◦C and 30 min as the optimal temperature and time for levulinic acid production, achieving a remarkable selectivity of 62.8% with the H-Beta zeolite catalyst using H_2O/WCPR = 10. Various properties of the resulting hydrochar are assessed, including higher heating values (HHVs), decarbonization (DC), dehydrogenation (DH), deoxygenation (DO), enhancement factor, carbon enrichment, surface area, pore diameter, weight loss as well as solid, carbon, hydrogen, and energy yields. The WT + Beta_220 sample, processed at 220 ◦C for 30 min, exhibited the highest HHV at 30.3 MJ/kg and carbon content at 78.9% in hydrochar compared to various biomass types, with an enhancement factor of 1.51 and carbon enrichment of 1.63, while the sequence of element removal during WT prioritized as DO > DH > DC. Furthermore, it is worth highlighting that the most significant weight loss, increasing from 17.0 to 60.7%, was observed under the same WT conditions. Lastly, a

comprehensive reaction pathway is proposed to elucidate the WT of WCPR with the presence of H-Beta zeolite catalyst under these optimized conditions. In light of the acquired product distribution data and a thorough analysis of the existing literature, an extensive reaction network has been constructed aimed at providing a clear depiction of the trans- formation of cellulose into a diverse array of valuable chemical products. This transformation is achieved through WT WCPR catalyzed by an H-Beta zeolite catalyst, and it encompasses the production of various compounds, prominently featuring levulinic acid, 5-HMF, hydroxyacetone, furfural, formic acid, acetaldehyde, ethanol, methanol, acetic acid, and others, as presented in **Figure 1.**

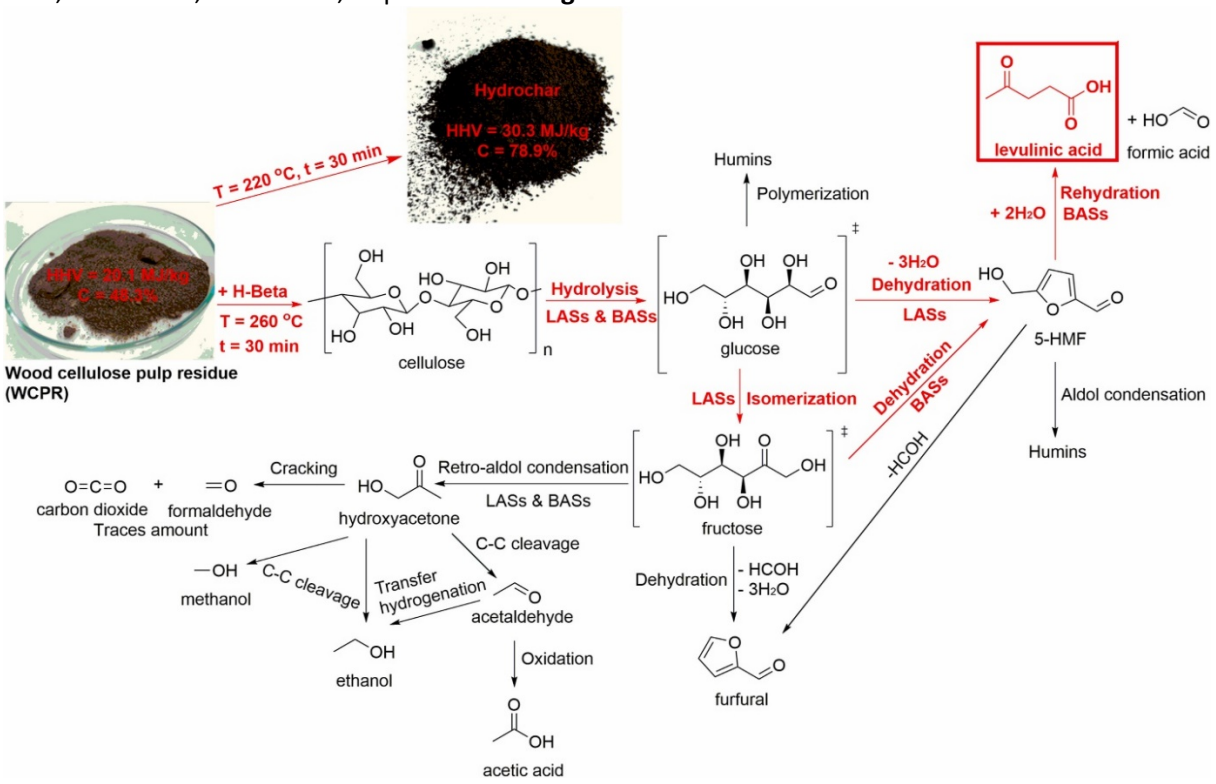


Figure 1. The reaction pathways for the WT of WCPR with H-Beta zeolite catalyst into hydrochar and the liquid value-added products.

References

[1] A. Kostyniuk, B. Likozar, *J. Clean. Prod.* **2024**, *449*, 141735.
[2] A. Kostyniuk, B. Likozar, *Chem. Eng. J.* **2024**, *485*, 149779.
[3] A. Kostyniuk, B. Likozar, *Renew. Energy* **2024**, *227*, 120509.
[4] A. Kostyniuk, B. Likozar, *Renew. Energy* **2024**, *226*, 120450.

Acknowledgements

The authors acknowledge financial support from CARBIOW (Carbon Negative Biofuels from Organic Waste) Research and Innovation Action funded by the European Commission under the Horizon Europe Programme with grant agreement ID: 101084443. The authors are also thankful to BioTrainValue (BIOmass Valorisation via Superheated Steam Torrefaction, Pyrolisis, Gasification Amplified by Multidisciplinary Researchers TRAINining for Multiple Energy and Products' Added VALUEs), with project number: 101086411 (Horizon Europe, Maria Skłodowska-Curie Staff Exchange).

Bimetallic LDHs origin catalysts containing Co, Fe and Ni for ammonia decomposition to hydrogen and nitrogen

Andrzej KOWALCZYK*, Lucjan CHMIELARZ
Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, Kraków, Poland.
** andrzej.kowalczyk@uj.edu.pl*

Significance and Relevance

In the presented studies, bimetallic systems Co-Ni, Fe-Ni and Co-Fe dispersed in MgO/Al_2O_3 matrix were obtained by calcination of layered double hydroxide (LDH) materials. Comparison of N_2-TPD profiles with the results of the catalytic tests showed a synergistic effect between metals leading to a decrease in the temperature of nitrogen molecules desorption and therefore in decreased recombination energy of adsorbed N atoms, which is postulated to be the rate-limiting step in the catalytic decomposition of ammonia to hydrogen.

Preferred and 2nd choice for the topic: H_2 storage and transportation, green H_2 production, hydrogen vectors. 2nd choice: Sustainable and clean energy production and transport.
Preferred presentation: Poster

Introduction and Motivations

Hydrogen is an environmentally friendly fuel, but for the most purposes its low volumetric energy density in a compressed gas makes its storage and transportation a serious problem. Compared to other potential hydrogen storage materials, ammonia has a high hydrogen storage capacity (17.6% by weight), energy density (3000 Wh/kg) and can be easily liquefied at 20 °C under the pressure of 0.8 MPa. These advantages of ammonia make it promising for hydrogen storage and transportation. Ruthenium-based catalysts for ammonia decomposition showed promising catalytic activities, and a Ru-supported on MgO/CNT and modified with alkali promoters showed the best activity at temperatures below 500 °C. The large-scale use of ruthenium based catalysts may not be feasible due to their high cost and scarcity. Studies on ruthenium catalysts have shown that their good catalytic activity results from the appropriate binding energy of N-metal. Transition metals such as Co, Ni and Fe have been reported to be effective catalysts for ammonia decomposition [1]. The main concept was to use a combination of two metals with nitrogen binding energies lower and higher than ruthenium to potentially mimic the chemical properties of ruthenium. Based on the nitrogen desorption energy, the potential bimetallic systems of Co-Ni, Co-Fe, Fe-Ni were selected for ammonia decomposition [2]. In addition, acidity and basicity of the supports used for deposition of the active metallic phase, play an important role in the customisation of efficient catalytic systems for the ammonia decomposition [3]. The layered double hydroxides (LDHs) offer great opportunities for synthesis of the catalysts with desired properties.

Materials and Methods

Two series of mixed metal oxides derived from layered double hydroxides (LDHs) with bimetallic compositions of transition metals Co-Fe, Co-Ni, and Fe-Ni were prepared as catalyst's precursors. The first series was prepared by direct synthesis of bimetallic system by the coprecipitation method. LDH materials containing Co/Fe/Mg/Al (HCoFe), Co/Ni/Mg/Al (HCoNi), Fe/Ni/Mg/Al (HFeNi) were synthesised. The second series of mixed metal oxides was prepared as follows. First, monometallic systems containing one of the transition metals (TM), such as Co (HCo), Fe (HFe), and Ni (HNi) were synthesised by the coprecipitation method. In the next step, the second metal was deposited on the calcined materials using the incipient wetness impregnation method. The following bimetallic materials: Co-Fe (HCo-iFe), Co-Ni (HCo-iNi), Fe-Co (HFe-iCo), Fe-Ni (HFe-iNi), Ni-Fe (HNi-iFe), and Ni-Co (HNi-iCo) were prepared by this method, where the first metal (in the sample code) denotes the metal introduced during the LDHs synthesis and the second metal (in the sample code) denotes the metal deposited by the incipient wetness impregnation method. All obtained materials were calcined in air at 600 °C for 12 hours and then reduced before the catalytic test at 800 °C in a flow of

pure hydrogen. The prepared catalysts were characterised by various methods, including: low-temperature N_2 adsorption-desorption, XRD, H_2-TPR, NH_3-TPD, N_2-TPD, TGA/DSC. The samples obtained were tested as catalysts for ammonia decomposition ($dcNH_3$) in the temperature range of 250 – 800 °C.

Results and Discussion

Figure 1A shows the results of catalytic tests for bimetallic CoFe, CoNi, and FeNi catalysts obtained from LDH materials, while Figure 2A presents the results of tests for bimetallic catalysts containing Co and Ni obtained by different methods. Figures 1B and 2B show the N_2-TPD results for the corresponding catalysts.

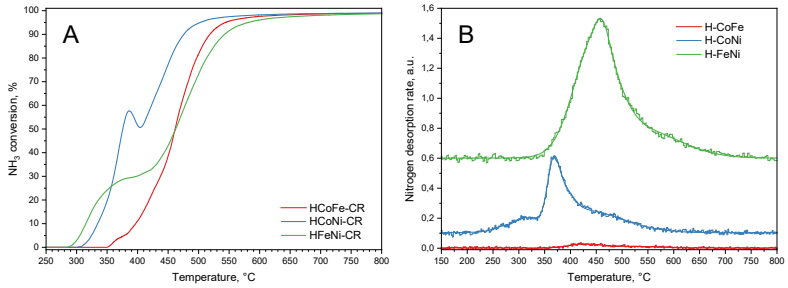


Figure 1. A - Results of catalytic tests for the LDHs-origined bimetallic CoFe, CoNi, FeNi catalysts calcined at 600 °C and then reduced at 800 °C. B - Results of N_2-TPD obtained for the same catalysts.

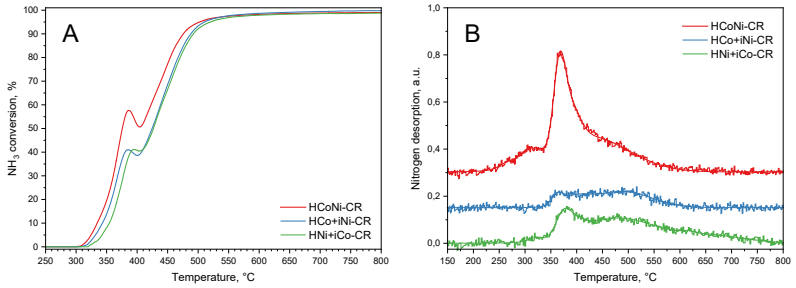


Figure 2. A - Results of catalytic tests for the bimetallic catalyst containing Co and Ni, prepared by different methods, calcined at 600 °C and then reduced at 800°C. B - Results of N_2-TPD for the same catalysts.

In the case of a series of bimetallic catalysts obtained from LDH materials, the best activity was obtained for catalysts containing Ni and Co. Comparison of the ammonia conversion profiles with the nitrogen desorption profiles showed a correlation between the nitrogen desorption temperature and catalytic activity. Nitrogen desorption profile for the HCoNi-CR catalyst begins at 225°C, the lowest temperature compared to the other catalysts, and finished at about 625°C, where the highest level of ammonia conversion was achieved among the catalysts tested in this series. However, the same analysis for the catalysts obtained by different orders of metallic components introduction showed that the HCoNi-CR catalyst (obtained by simultaneous coprecipitation of both metals) resulted in better catalyst than those obtained by depositing of the second metal by impregnation method.

References

1. A. Boisen, S. Dahl, et. al., *Journal of Catalysis* **2005**, 230, 309
2. E. Medina, C. Fernández, et. al., International Journal of Hydrogen Energy **2024**, 90, 1435
3. A. Kowalczyk, M. Rutkowska, S. Gnyla, M. Pacia, L. Chmielarz, ChemEngineering **2024**, 8, 55.

Acknowledgements

The research has been supported by a grant from the Faculty of Chemistry under the Strategic Programme Excellence Initiative at Jagiellonian University.

Impact of electroplating parameters on palladium hydride phases and hydrogen desorption dynamics

Elena MARIANI[1,2,3*], Margherita VERRUCCHI[1], Ambra PELAGATTI[1], Fabio BIFFOLI[1], Walter GIURLANI[1,2], Pierandrea LO NOSTRO[1], Marco PAGLIAI[1], Massimo INNOCENTI[1,2]

[1] *Department of Chemistry, UNIFI, via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy.*

[2] *INSTM, via Giuseppe Giusti, 9, 50121, Florence (FI), Italy.*

[3] *Eco-Tech Finish s.r.l., Z.I. San Zeno, Strada C 27, 52100 Arezzo, AR, Italy.*

** elena.mariani@unifi.it*

Significance and Relevance

The study explores the formation of palladium hydrides during electroplating, finding that current density and deposit thickness influence hydrogen content and phase stability. XRD analysis revealed that β-PdH_x predominates at low current densities, while α-PdH_x is favored at high currents. Pulsed and reverse currents significantly altered the deposit morphology and hydrogen retention. Compact deposits, retained hydrogen in the β-phase even after 24 hours, showing potential for hydrogen storage. These results provide a new approach to palladium hydride phase control for specific uses such as the energy field.

Preferred and 2nd choice for the topic: H_2 storage and transportation, green H_2 production, hydrogen vectors; circular economy

Preferred presentation: Poster

Introduction and Motivations

The study investigates palladium electroplating, widely used in decorative and industrial applications due to its corrosion resistance and aesthetic properties[1,2]. Challenges such as hydrogen-induced microfractures and phase transitions (α-β) impact deposit quality and limit practical uses[3]. Understanding the influence of deposition parameters on hydrogen incorporation and phase stability could improve both decorative and hydrogen storage applications[4]. Additionally, β-PdH_x offers potential for solid-state hydrogen storage, a safer alternative to compressed gas[5]. This motivates optimizing electroplating techniques to tailor palladium deposits for specific functional and aesthetic requirements.

Materials and Methods

The study used a commercial palladium-iron (PdFe) electroplating bath containing proprietary additives and 3 g/L $Pd(NH_3)_2(NO_2)_2$. Brass substrates were electrodeposited with palladium under direct (DC), pulsed (PC), and reverse pulsed currents (PRC) across varying current densities and thicknesses. X-ray diffraction (XRD) identified palladium hydride phases and their desorption over time, while scanning electron microscopy (SEM) and atomic force microscopy (AFM) analyzed deposit morphology. X-ray fluorescence (XRF) measured thickness, and colorimetric analysis assessed surface gloss and hydrogen-related changes.

Results and Discussion

The study investigated the impact of electrodeposition parameters on palladium (Pd) deposits, focusing on hydrogen absorption and desorption. The X-ray diffraction (XRD) analysis revealed two palladium hydride phases, β-PdH_x and α-PdH_x, with the β-phase (hydrogen-rich) forming at lower current densities and the α-phase (hydrogen-poor) at higher current densities. The desorption rate of hydrogen from the Pd deposits was studied over time, showing a transition from β to α phase, depending on current density and thickness. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) revealed morphological differences in the deposits.

The findings provide valuable insights into controlling palladium hydride formation for hydrogen storage and electroplating applications. The ability to modulate the hydrogen content and desorption

rate by adjusting the deposition parameters opens the door for optimizing palladium-based deposits in both decorative and energy storage sectors.

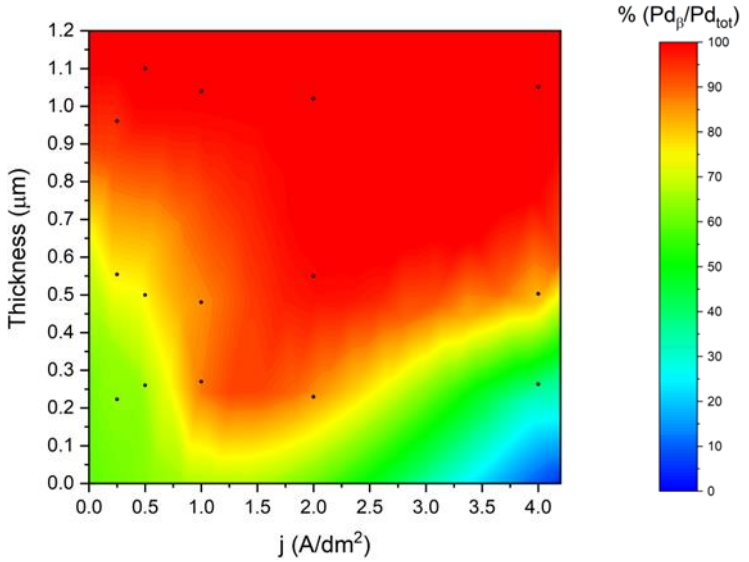


Figure 1 β-PdH_x percentages obtained on DC samples after 10 minutes after the end of deposition. The black dots represent the samples.

References

1. K. M. Chow, W. Y. Ng, L. K. Yeung, *Surface and Coatings Technology*, **1998**, *105*, 56-64.
2. F. Biffoli et all, *Heliyon*, **2024**, *10*, e32147.
3. F. D. Manchester, A. San-Martin, J. M. Pitre, *Journal of Phase Equilibria*, **1994**, *15*, 62-83.
4. J. D. Benck et all, *Chemistry of Materials*, **2019**, *31*, 4234-4245.
5. G. Abbondanza et all, *Nanotechnology*, **2023**, *34*, 505605.

Acknowledgements

The authors thank for the support offered by Fondazione CR Firenze, Fondazione per la Ricerca e l'Innovazione dell'Università degli Studi di Firenze and Confindustria Firenze within the FABER 4 project.
Authors also acknowledge Regione Toscana PR FESR 2021/2027, Azione 1.1.4.1, Bando 2 "Progetti di ricerca e sviluppo per le MPMI e Midcap" which made possible the project "Processo Unificato su Leghe di zama, ottone e alluminio, Sicuro e Ecofriendly" (P.U.L.S.E) CUP-ST 27717.29122023.043000271.

Electrodeposition of nanostructured metals on silicon. A focus on the rhodium/n-doped silicon composite as a promising platform for energy applications

Francesco Montanari*[1], Giulio Pappaianni[1], Francesco Visconti[1], Patrick Nunziati[1], Walter Giurlani[1,2], Massimo Innocenti[1,2]

[1]*University of Florence, Department of Chemistry "Ugo Schiff", via della Lastruccia 3-13, Sesto Fiorentino 50019, Italy.*

[2] *National Interuniversity Consortium of Material Science and Technology (INSTM), 50121, Italy.*

** francesco.montanari@unifi.it*

Significance and Relevance

The work demonstrates the successful electrodeposition of nanostructured metals, with a focus on rhodium, on n-doped silicon. High surface coverage (up to 84%), tunable particle sizes (57-168 nm) and controlled morphology were achieved using multi-cycle charge-controlled deposition. Rhodium electrodeposition on silicon is scarcely reported in the literature and these results could improve applications in energy-related fields, including catalysis for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in water splitting devices.

Preferred and 2nd choice for the topic: H_2 storage and transportation, green H_2 production, hydrogen vectors and sustainable and clean energy production and transport

Preferred presentation: Poster

Introduction and Motivations

In light of the escalating energy crisis and environmental concerns, there is an urgent need for clean and sustainable energy-related materials and related storage and conversion devices[1]. The deposition of thin metal films or patterns and nanostructured metal materials on silicon substrates holds significant technological importance as it offers a unique opportunity to blend the advantageous characteristics of metals with the exceptional electronic properties of silicon. This combination is pivotal for developing advanced technologies in energy storage, hydrogen production, catalysis, photovoltaics, and sensing[2]. To achieve this object the electrodeposition technique was selected. The advantage of this technique over others such as physical vapor deposition (PVD) or chemical vapor deposition (CVD), at the state of art, is that it is performed at room temperature and atmospheric pressure in aqueous solution, making it inexpensive and easily scalable[3].

Results and Discussion

The initial selection of metals for the electrodeposition on the silicon substrate was conducted through the study of the data obtained from computational calculations thanks to The Open Quantum Materials Database (OQMD) based on Density Functional Theory (DFT) at the PBE/PAW level. Voltammetric studies were then carried out using solutions containing Ni, Ru, Pd, Rh, Pt, Ag, Mn, and Co. Charge-controlled depositions were performed, and tests on electroless deposition were made. The deposits obtained were characterized morphologically and compositionally using Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectroscopy Analysis (EDS).

Following this preliminary study rhodium turned out to be the most promising metal among those selected according to the characterization accomplished.

Focusing on rhodium electrodeposition a high surface coverage (up to 84%), tunable particle sizes (57-168 nm) and controlled morphology were achieved using multi-cycle charge-controlled deposition. Additionally, X-ray Photoelectron Spectroscopy (XPS) demonstrated the presence of a rhodium deposit in a purely metallic form. The advances presented in this work address a notable gap in the literature on rhodium electrodeposition on silicon and offer significant potential for energy-related applications. For instance, a rhodium-silicon platform could be significant for HER catalysis as reported in the literature[4], since it separates hydrogen adsorption (on Rh) and desorption (on Si), overcoming Sabatier's principle limitations and achieving higher efficiency and stability than platinum-based catalysts at high current densities.

Obtaining a silicon surface with a higher surface area might be useful for future developments to enhance its catalytic activity.

Therefore the knowledge gained was used to realize ultrathin silicon nanowires (NWs) using a procedure, at the state of the art, not widely used in the literature consisting in a wet etching process assisted by an electrochemically deposited metal thin film.

By providing an efficient, scalable, and cost-effective alternative to traditional vapor-phase methods, this work paves the way for the building up of composites presenting enhanced catalytic performance in various hydrogen fields, such as the hydrogen evolution reaction (HER), contributing to the development of sustainable energy.

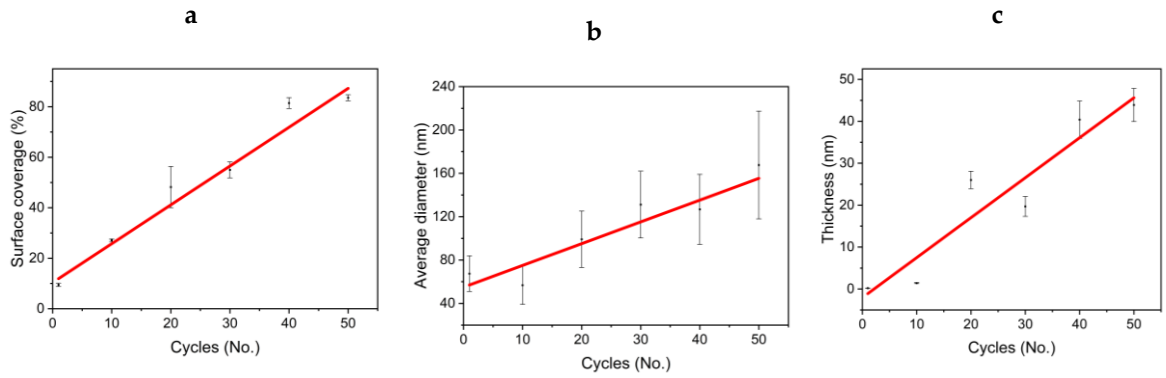


Figure 1: a) Surface coverage trend; b) average particles diameter size trend; c) equivalent thickness trend of the deposits, obtained through a variable number of charge controlled deposition cycles (1, 10, 20, 30, 40, and 50 cycles) on Si working electrode using H_2SO4 0.1 M, $RhCl_3$ 1mM solution.

References

1. Wan, H. *et all*, *Green Energy Environ.* **2022**, 7, 205-220.
2. Sulka, G.D., **2023**, *Molecules* 28, 4040.
3. Zeng, X., Zhao, Y., Hu, X., Stucky, G. D. & Moskovits, *Small Struct.*, ***2021***, 2, 2000138.
4. Zhu, L. *et al.*, *Nat. Commun.*, **2016**, 7, 12272.

FROM SEWAGE SCUM UP TO LIPIDS PRODUCTION USING OLEAGINOUS YEASTS AS BIOCATALYSTS

Nelly MORRONE*[1], Nicola DI FIDIO[1], Valeria D'AMBROSIO[2], Claudia ANTONETTI[1], Anna Maria RASPOLLI GALLETTI[1], Carlo PASTORE[2]

[1]*Department of Chemistry and Industrial Chemistry, University of Pisa, Via G. Moruzzi 13, 56124 Pisa, Italy*

[2]*Water Research Institute (IRSA), National Research Council (CNR), Viale De Blasio 5, 70132 Bari, Italy*

**nelly.morrone@dottorandi.unipg.it*

Significance and Relevance

For the first time, the fermentation of undetoxified sugar-rich sewage scum hydrolysate, a special waste separated during municipal wastewater treatment, was successfully achieved using a promising commercial yeast to produce microbial oil. One of the most critical factors affecting its cost production is the feedstock; therefore, using low-cost or even negative-value waste resources, such as sewage scum, could significantly reduce its manufacturing price and, consequently, that of the obtained biodiesel and fine oleochemicals. Moreover, the valorization of the sewage scum would lower the disposal expenses of this waste, also reducing its environmental concerns, in agreement with Green Chemistry principles.

Preferred and 2nd choice for the topic: 1. Green chemistry and biomass transformation, renewable resources conversion, 2. Circular economy; Preferred presentation: Oral preferred or Short Oral.

Introduction and Motivations

Recently microbial oils, namely single cell oils (SCOs), have gained significant attention as third-generation raw materials for producing biodiesel and fine oleochemicals. Among oleaginous microorganisms able to produce SCOs, yeasts are the most promising lipid-accumulating microbes, due to their ability to grow fast, independently from environmental conditions, and to utilize a wide range of carbon sources, including low-cost substrates, such as wastes, thus enhancing the economic and ecological feasibility of the industrial implementation of oil production[1]. Among the various types of wastes generated globally, sludge from municipal wastewater treatment plants (WWTPs) is receiving significant attention due to its high carbon content and nutrient composition that oleaginous yeasts can use for cell growth and lipid accumulation, including cellulose, proteins and organic acids[2]. Sewage scum (SS) is a special waste easily recoverable from WWTPs through preliminary flotation of urban sewage, and, at the moment, it is disposed of in landfills as a wet material. SS contains a polysaccharide fraction (mainly made up of cellulose, sourced from toilet paper, and hemicellulose), in addition to the more substantial lipid fraction[3]. Therefore, a promising alternative for valorizing this kind of wastewater sludge is its use as a carbon source for the growth of selected oleaginous yeasts in order to produce a new generation oil, suitable for biofuels and fine oleochemicals production. On this basis, the aim of this work, carried out in line with the goals of the national ReFil PRIN 2022 Project, was the fermentation of the hydrolysate obtained through the enzymatic hydrolysis of SS, containing mainly glucose and xylose, in the presence of oleaginous yeasts in order to valorize the SS waste. This innovative approach, which has not been explored so far, not only represents a novel contribution to the field, but also addresses two critical challenges simultaneously: the reduction of the cost of lipid production and the decrease of environmental and economic impacts associated with SS disposal.

Materials and Methods

The chemical composition of SS was initially determined, focusing on total solid content, easily hydrolysable sugars, cellulose, proteins, lignin, humic compounds and trans-esterifiable lipids. The analysis revealed that cellulose was the predominant component, accounting for 52.9 wt%. Therefore, in order to produce fermentable sugars, the enzymatic hydrolysis of SS was carried out in water in the presence of the commercial enzyme mixture Cellic® CTec 2 (dry sludge loading of 10 wt%, 24 FPU/g substrate, 50 °C, 72 h). The enzymatic hydrolysate of SS (SSH) resulted in a suspension, which was

centrifugated (4000 rpm, 10 min). The liquid phase of SSH was characterized through HPLC analysis and selected as the substrate for the growth of oleaginous yeasts, due to its high sugars concentration (44.1 g/L glucose, 9.3 g/L xylose). Different commercial oleaginous yeasts, *Cryptococcus curvatus*, *Trichosporon oleaginous* and *Rhodosporidium toruloides,* were grown on a synthetic culture medium (SM), used as a model, and the most effective one was selected as the biocatalyst for fermenting SSH, using the same optimized process conditions adopted during the previous screening on SM. SM was characterized by a sugar composition (glucose and xylose) identical to that of the SSH, while all batch-mode fermentative processes were carried out by adapting the operating conditions described in our previous work[1]. To assess the impact of the C/N ratio on lipid accumulation, three different C/N ratios (80, 100, and 120 g/g) were tested on SSH. Finally, the SCOs obtained from all the fermentations were characterized by GC-MS analysis. Based on the obtained FAMEs profile, several chemical and physical parameters of the produced biodiesel were calculated to predict its quality.

Results and Discussion

The preliminary experimental results on SM confirmed that the best oleaginous yeast among those tested was *T. oleaginosus* due to its very high lipid cell content (66.7 wt%), productivity (168.0 mg $L^{-1}h^{-1}$) and lipid yield (22.6 wt%, equal to 68.5 wt% of the theoretical lipid yield). On this basis, this yeast was selected as the biocatalyst for the fermentative process of the undetoxified SSH (Figure 1). *T. oleaginosus* was able to grow on SSH and completely consume glucose and xylose in a slightly longer reaction time (96 hours) compared to the fermentation on the SM (72 hours). This difference can be explained taking into account that the microorganism needs to adapt itself to the particularly complex substrate, as evidenced by the starting lag phase in the growth curve. Adopting the optimal C/N ratio (80 g/g), this bioprocess enabled us to achieve 45.6 wt% of lipid accumulation, together with a lipids productivity and yield of 83.3 mg $L^{-1}h^{-1}$ and 15.0 wt%, respectively. These results are quite similar to those achieved by the fermentation of SM by the same biocatalyst, confirming the versatility and adaptability of *T. oleaginosus* in complex and unconventional substrates, such as SS, creating as a consequence, new opportunities for the valorization of those underutilized waste streams. Finally, the lipid profile characterization of all SCOs obtained in the present investigation highlighted that the composition of these oils were very similar to those of common vegetable oils, employed at the industrial scale for commercial applications, including the production of traditional biodiesel.

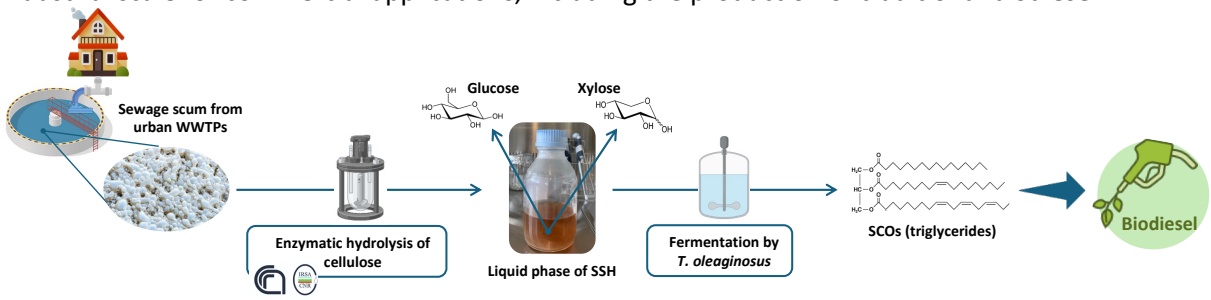


Figure 1. Process scheme of the production of SCOs from sewage scum through separated enzymatic hydrolysis and fermentation in the presence of the yeast *Trichosporon oleaginous* as biocatalyst.

References

1. N. Di Fidio, F. Dragoni, C. Antonetti, I. De Bari, A. M. Raspolli Galletti, G. Ragaglini, *Bioresource Technology* **2020**, *315*, 123790-123798.
2. S. Singh, D. Kumari, A. Daverey, K. Dutta, *Advances in Yeast Biotechnology for Biofuels and Sustainability* **2023**, 129-165.
3. L. di Bitonto, A. Lopez, G. Mascolo, G. Mininni, C. Pastore, *Renewable Energy* **2016**, *90*, 55-61.

Acknowledgements

The authors thank the PRIN 2022-Project ReFil “Renewable liquid Fuel of new generation from wastewater sludge: a step towards circular economy” funded by the European Union-Next Generation EU, Mission 4 Component 1 (code 2022KA5WL8, CUP I53D23001790006).

Durable Ethane Oxidation to Ethanol: Insights into SMSI Effects on TiO_2-Supported Pt Catalysts

Akira Oda[*,1], Terufusa Inagaki[1], Koyo Ichino[1], Yuta Yamamoto[2], Yuya Kimura[1], Kyoichi Sawabe[1], Atsushi Satsuma[1]

[1]*Department of Materials Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan.*

[2] *Institute of Materials and Systems for Sustainability, Nagoya University, Nagoya 464-8603, Japan.*

**Corresponding author email: akira@chembio.nagoya-u.ac.jp*

Significance and Relevance

The direct oxidation of ethane to ethanol using a durable and selective catalyst represents a promising avenue for sustainable chemical synthesis, with significant implications for the energy and chemical industries. Here, we present an anatase-TiO_2-supported PtTi alloy catalyst, which achieves over 50% ethanol selectivity while maintaining stable catalytic performance for over 48 hours at 125°C. Strong metal-support interactions (SMSI) between Pt and TiO_2 were induced to create PtTi alloy sites, endow resistance to CO-induced deactivation, enabling continuous ethanol production.

Introduction and Motivations

Ethanol, a versatile fuel and feedstock, is conventionally derived through multi-step and energy-intensive processes, primarily from ethane. A direct, single-step catalytic oxidation approach promises a more sustainable and energy-efficient alternative, yet achieving high activity, selectivity, and durability remains challenging. Inspired by natural enzymatic oxidation pathways, our group recently developed a CO-assisted conversion of ethane to ethanol using a Pt-based catalyst, breaking the activity-selectivity tradeoff established so far.[1] However, CO-induced aggregation and deactivation of supported Pt limit prolonged application. This study explores the potential of SMSI to develop sinter-resistant Pt-based catalysts. SMSI frequently induces modification of the surface structure of the supported Pt via interaction with support elements, weakening the interaction with CO and preventing the aggregation of supported Pt nanoparticles.[2]

Materials and Methods

The catalyst was prepared by impregnating a Pt(II) nitrate solution onto anatase-TiO_2, followed by hydrogen reduction at 300 or 700 °C, tuning the degree of MSI. These catalysts are denoted as H300, and H700, respectively. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), X-ray absorption fine structure (XAFS), and diffuse reflectance infrared Fourier transform spectroscopy using CO as a probe molecule (CO-DRIFTS) were applied to examine the structure and electronic states of supported Pt species. Activity test was conducted in a high-pressure batch reactor at 125 °C under 1 MPa ethane, 0.24 MPa CO, and 0.08 MPa O_2.[1]

Results and Discussion

HAADF-STEM images of H300 and H700 are shown in **Figure 1a**. Based on the analyzed lattice spacing and lattice orientations, it was confirmed that Pt and PtTi nanoparticles are formed in H300 and H700, respectively, indicating that high-temperature reduction leads to alloying Pt nanoparticles with reduced TiO_2 surface; that is, SMSI occurred. Wavelet transform of extended XAFS demonstrated that the (k, R) coordinate for Pt–O and Pt–Pt backscattering shifted in response to the SMSI effect, and Pt-Ti backscattering was detected, supporting the formation of PtTi alloy nanoparticles. **Figure 1b** shows CO-DRIFT spectra of H300 and H700 before the reaction (dash lines, denoted as “fresh”). H300 gave a dominant ν_{CO} band at 2079 cm^{-1} attributed to CO adsorption via atop mode. On the other hand, H700 gave no band except for the gas-phase CO signals, which is the typical signature of SMSI.

Figure 1c,d shows the time course of turnover number (mole of liquid-phase product normalized with mole of Pt) and selectivity in ethane oxidation by H300 and H700. For H300, TON increased only up to 12 hours. On the other hand, H700 catalyzed continuous ethanol production with selectivity exceeding

50% over a 48-hour period. These results indicate that the SMSI-assisted surface modification of Pt nanoparticles contributes to the suppression of deactivation. Arrhenius plot was obtained in the 24h reactions using H700 (**Figure 1e**), demonstrating the durable catalysis in ethane oxidation. The apparent activation energy was determined to be 41.6 kJ/mol. The low E_a value indicates that the PtTi alloy can sustain efficient catalytic activity at low temperatures.

HAADF-STEM images after 48 hours showed that H700 retained a distribution of particle size similar to its initial state, while H300 showed extensive particle growth. CO-DRIFT spectra for spent H700 catalyst provided ν_{CO} bands appeared at 2098, 2082, and 2047 cm^{-1} which are assignable to CO adsorbed on $Pt^{\delta+}$, Pt^{0}, and PtTi alloy sites, respectively (**Figure 1b**, solid line). These are indicative that surface modifications further occur during the reaction with the evolution of $Pt^{\delta+}$-Pt^{0} dual-site. In our previous, the $Pt^{\delta+}$-Pt^{0} dual-site was proposed as the active site in facilitating the oxidation of ethane to ethanol.[1] On the other hand, H300 provided only ν_{CO} band attributed to CO adsorbed on Pt nanoparticles via atop mode; no spectroscopic evidence for $Pt^{\delta+}$-Pt^{0} dual-site was obtained.

In summary, SMSI-induced PtTi alloys created CO-resistant surfaces with $Pt^{\delta+}$-Pt^{0} dual sites, enabling prolonged catalytic oxidation of ethane to ethanol.

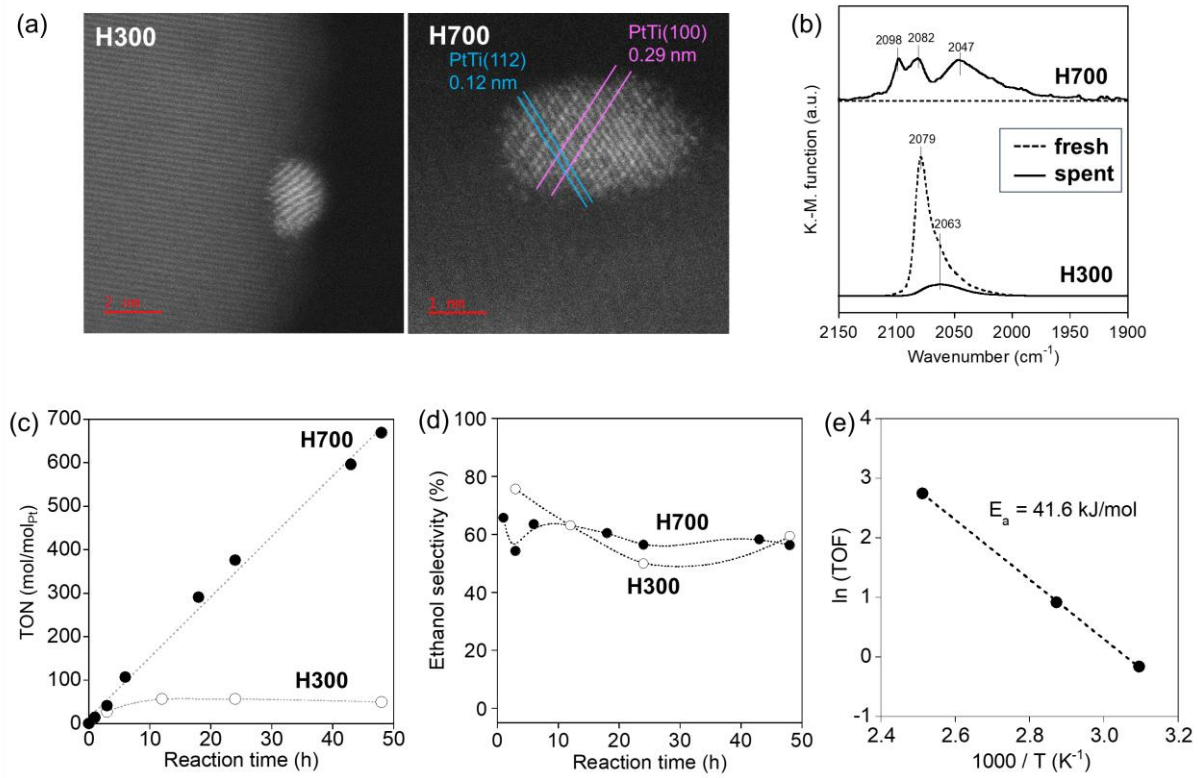


Figure 1 (a) HAADF-STEM images. (b) CO-DRIFT spectra. Time course of (c) TON and (d) ethanol selectivity. (e) Arrhenius plot.

References

1 A. Oda, Y. Kimura, K. Ichino, Y. Yamamoto, J. Kumagai, G. Lee, K. Sawabe, A. Satsuma, *J. Am. Chem. Soc.* **2024,** *146*, 20122–20132.

2 W. He, X. Zhang, K. Zheng, C. Wu, Y. Pan, H. Li, L. Xu, R. Xu, W. Chen, Y. Liu, C. Wang, Z. Sun, S. Wei, *Angew. Chem. Int. Ed.* **2023,** *62*, e202213365.

Acknowledgements

This work was supported by the JGC-S Scholarship Foundation, the Japan Society for the Promotion of Science (JSPS) Grant-in-Aid for Scientific Research (B) (No. 22H01866 and No. 23H01759), and JSPS Grant-in-Aid for Transformative Research Areas (B) (No. 22H05045). The XAFS measurements were performed at the Aichi synchrotron radiation center.

Promotion Effect of Water Vapor on co-Adsorption of NO on Pd/Zeolite

Takeshi OHTSU[1], Nao TSUNOJI[2], Akira ODA[1], Atsushi SATSUMA[1]*
[1]*Nagoya University, Department of Materials Chemistry, Furo-cho, Chikusa-ku, Nagoya, Japan.*
[2] *Hiroshima University, Department of Applied Chemistry, Kagamiyama 1-4-1, Higashi-hiroshima, Japan.*
** satsuma@chembio.nagoya-u.ac.jp*

Significance and Relevance

It is known that H_2O inhibits low temperature NO adsorption on Pd/zeolite as a Passive NOx Adsorber (PNA). This study discovered that supplying NO and H_2O at 150°C increased the amount of NO adsorbed on Pd/zeolite. The increase in NO adsorption due to H_2O was confirmed in multiple zeolite structures. Observation of the adsorbed species by in-situ FT-IR analysis revealed that the NOx adsorption state changes depending on the NO concentration.

Introduction and Motivations

The selective catalytic reduction (SCR) catalysts are effective for lowering NOx emissions from lean-burn diesel engines above 200 °C. However, with the advancement of engine efficiency, NOx reduction at lower temperatures, such as during cold start below 200°C, is strongly required. One of the approaches to suppress NOx emissions at low temperatures is the Passive NOx Adsorber (PNA). The PNA is positioned upstream of the SCR, adsorbs NOx at low temperatures, and releases NOx within the active temperatures of the SCR catalyst. Among various PNA materials, Pd-loaded zeolites are considered the most promising candidates due to their high NOx adsorption efficiency and superior SOx resistance[1]. However, challenges remain in preventing the reduction of NOx adsorption capacity due to H_2O adsorption in the exhaust gas[2]. Previous studies have reported that the coexistence of CO enhances NO adsorption even in the presence of H_2O[3]. In this study, we discovered a unique phenomenon that NOx adsorption capacity increases when NO and H_2O were simultaneously supplied to Pd/zeolite.

Materials and Methods

The Pd/zeolite used in this study (Pd/zeolite code - Si/Al ratio) was prepared by loading 1 wt% Pd onto NH_4-type zeolite using the impregnation method, followed by calcination at 600°C for 30 minutes and subsequent steam treatment at 750 °C for 8 hours. The NOx adsorption capacity of the Pd/zeolite was measured by NOx-TPD (temperature-programmed desorption). The NOx-TPD profile was obtained by pre-treating the Pd-zeolite at 600 °C in a 10% O_2/Ar flow for 15 minutes, followed by NOx adsorption at 150 °C by supplying 1020 ppm NO/10% H_2O (if used)/8% O_2/Ar for 1 hour. After that, the sample was purged with Ar for 1 hour to remove physically adsorbed species, and then the temperature increased from 150 to 500 °C at a rate of 5 °C/min under an 8% O_2/Ar flow. To observe NOx adsorption species, in-situ FT-IR spectra were measured using a JASCO FT/IR-6100.

Results and Discussion

Figure 1 shows the NOx adsorption capacity when NO was adsorbed on Pd/zeolites with different structures. In Pd/BEA-13.6, the NOx adsorption capacity decreased when H_2O was introduced during NO adsorption. the in-situ IR results confirmed that no bands attributed to NOx adsorption species were formed on Pd/BEA-13.6 when 1020 ppm NO and 10% H_2O were introduced simultaneously. These results indicate that Pd/BEA-13.6 exhibits a decrease in NOx adsorption capacity due to H_2O, as reported in previous studies[4]. On the other hand, Pd/CHA-13 exhibited an increase in NOx adsorption capacity in the presence of H_2O. This phenomenon has only been reported in a limited number of cases, such as in Pd/FER[5]. Notably, this study revealed that the enhancement of NOx adsorption capacity induced by H_2O is observed not only in Pd/CHA-13 but also across various framework structures. Furthermore, the increase in NO adsorption due to H_2O did not occur unless NO and H_2O were introduced simultaneously to the Pd/zeolite. This suggests that changes in the adsorption state due to the presence of both NO and H_2O influence the NOx adsorption capacity.

Figure 2 shows the NOx adsorption capacity and the in-situ FT-IR spectra during NO adsorption when varying the NO concentration supplied with H_2O on Pd/CHA-13. In Pd/CHA-13, the NOx adsorption capacity increased in the presence of H_2O at any NO concentration. The NOx adsorption capacity varied depending on the concentration of NO adsorbed. The NOx desorption temperature also showed different results depending on the concentration of NO adsorbed. The differences in NOx adsorption and desorption behavior depending on NO concentration indicate that there are distinct NO adsorption states.

The in-situ FT-IR results for NO adsorption on Pd/CHA-13 showed NO-derived bands in the range of 1700–1900 cm^{-1}. When H_2O was absent, bands near 1858 cm^{-1} and 1810 cm^{-1} were observed, attributed to Pd^{2+}-NO and Pd^{+}-NO, respectively[5-7]. In the absence of H_2O, there was no change in NOx adsorption capacity, and significant changes in adsorption species were not observed. On the other hand, when H_2O was present, bands at 1803 cm^{-1} and 1750 cm^{-1} were observed, attributed to $Pd^{2+}(NO)(H_2O)_x$ and $Pd^{+}(NO)(H_2O)_x$, respectively[5-7]. At 500 ppm NO, bands at 1862 cm^{-1} and 1842 cm^{-1} were observed, corresponding to Pd^{2+}-NO and $[Pd(OH)]^{+}$-NO, respectively[4,7], while at 1020 ppm NO, the band at 1803 cm^{-1} was more dominant. These results suggest that higher NO concentrations allow co-adsorption of NO and H_2O on Pd cations, indicating that NOx adsorption and desorption behavior varies depending on the adsorption state influenced by NO concentration.

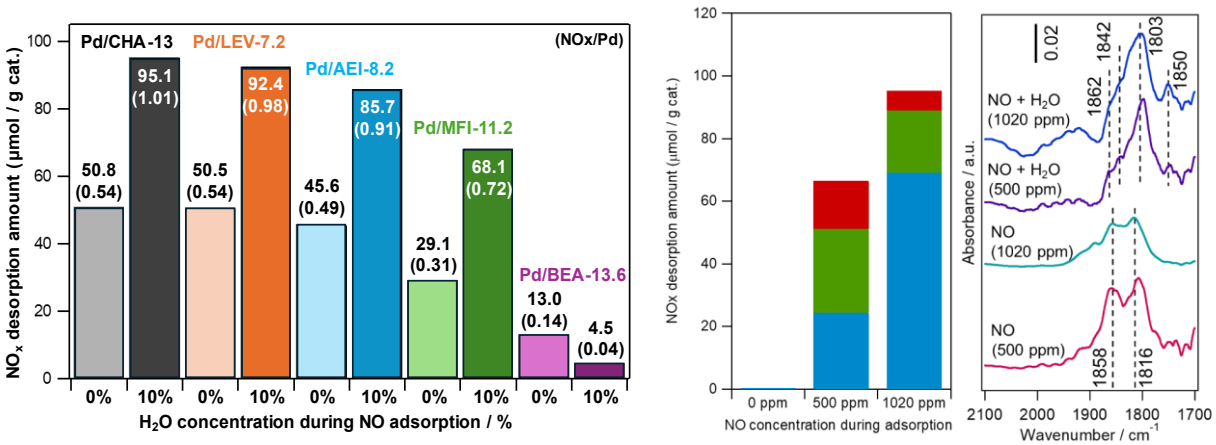


Fig.1 (left) NOx desorption amount per catalyst weight of Pd/zeolites calculated from NOx-TPD profiles. NO adsorption conditions: 150°C, 1020 ppm NO, 10% H_2O (if used), 8% O_2/Ar, 50 mL/min (GHSV=20000 h^{-1})

Fig.2 (right) (a) NOx desorption amount of Pd/CHA-13. (b) In-situ FT-IR spectra of NO adsorption state after 30 minutes of NO adsorption. Both of NO adsorption conditions: 150°C, 1020 ppm NO, 10% H_2O, 8% O_2/Ar, 50 mL/min (GHSV=20000 h^{-1})

References

1. H.Y.Chen et al., *Catal Lett.* 146, 1706 (2016).
2. A. Porta et al., *Top Catal* **61**, 2021 (2018).
3. K. Khivantsev et al., *Appl Catal B* **280**, 119449 (2021).
4. Y. Wang et al., *Appl Catal A* **672**, 119605 (2024).
5. I. Song et al., *Appl Catal B* **318**, 121810 (2022).
6. R. Matarrese et al., *Appl Catal B* **331**, 122723 (2023).
7. Y. Liu et al., *ACS Omega* **9**, 30452 (2024).

Acknowledgments

This work is based on the results of JPNP14004, a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO) and entrusted to The Research Association of Automotive Internal Combustion Engines (AICE).

Decomposition of model organic pollutants via wet peroxidation – the activity of composite copper catalysts in the generation of ROS

Wiktor CZERWONKA[1], Kamila SOBAŃSKA[1], Piotr PIETRZYK[*,1]
[1]*Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, 30-387 Krakow, Poland.*
** piotr.pietrzyk@uj.edu.pl*

Significance and Relevance

Due to the constantly increasing level of water pollution with organic substances, special attention has been paid to the development of new catalysts for the degradation of these pollutants through advanced oxidation processes (AOP) in recent years. These processes are based on the generation of reactive oxygen species (ROS), including hydroxyl radicals (•OH) and singlet oxygen ($^1O_2$), which enable the degradation of contaminants into simpler, less harmful forms and, in some cases, complete mineralization.

Preferred and 2nd choice for the topic: Water treatment, Fundamental advances in understanding catalysis
Preferred presentation: Poster

Introduction and Motivations

The generation of reactive oxygen species (ROS) can occur via various mechanisms such as the Fenton reaction and its modifications or the electroprotic pathway. The former requires redox-active centers, whereas the latter relies on acid–base functional groups that mediate the coupled transfer of electrons and protons. The integration of these two mechanisms in a material can be achieved by synthesizing a composite catalyst composed of two types of oxide materials: a crystalline, redox-active phase and an amorphous, hardly reducible phase.[1]

The aim of this study is to develop a composite material in which the active phase comprises copper inorganic compounds. The materials include CuO_x, CeO_2, Nb_2O_5 single oxides, mixed Cu-Ce oxides, as well as selected copper hydroxo nitrate compounds. In the context of Fenton-like reactions, the Cu(II)/Cu(I) redox cycle is thermodynamically more favorable than the conventional iron ion cycle. Moreover, copper ion complexes are generally less stable than iron(III) complexes, which reduces the probability of permanent deactivation of the catalytic sites.

Results and Discussion

This work investigates potential catalysts for hydrogen peroxide decomposition and ROS generation. Each material was subjected to structural analysis using X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS/EDX). Additionally, X-ray photoelectron spectroscopy (XPS) was employed to analyze the surface elemental speciation. These measurements enabled the assessment of crystallinity, phase composition, morphology, and elemental composition of the synthesized samples. The capacity of the materials to generate hydroxyl radicals (•OH) and singlet oxygen ($^1O_2$) from H_2O_2 decomposition was evaluated using electron paramagnetic resonance (EPR) spectroscopy, in combination with the spin trap 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and the reactive probe 2,2,6,6-tetramethyl-4-piperidone (TEMPD) (**Figure 1a**). The chemical activity and potential applicability of the synthesized materials in advanced oxidation processes (AOPs) were evaluated through a model degradation reaction of the water pollutant, Direct Blue 15 (DB15) dye (**Figure 1b**).

The obtained results indicate that catalysts comprising two distinct metals with redox properties (Cu, Ce) exhibit the highest activity in the dye degradation process. It has been demonstrated that the concurrent presence of copper in multiple oxidation states has a significant impact on the activity of Fenton-like catalysts. Moreover, incorporating a minimal amount of the redox-active phase into the support material that exhibits an electroprotic mechanism of ROS generation (Nb_2O_5) significantly increases its catalytic efficiency. In addition, by promoting the Cu-based materials with Ce, one changes

not only the overall reactivity of the catalysts, but also the distribution of particular ROS (see **Figure 1a**), which have been identified by EPR as hydroxy radicals (characteristic of Cu-based materials) and singlet oxygen (Cu-Ce-based materials).

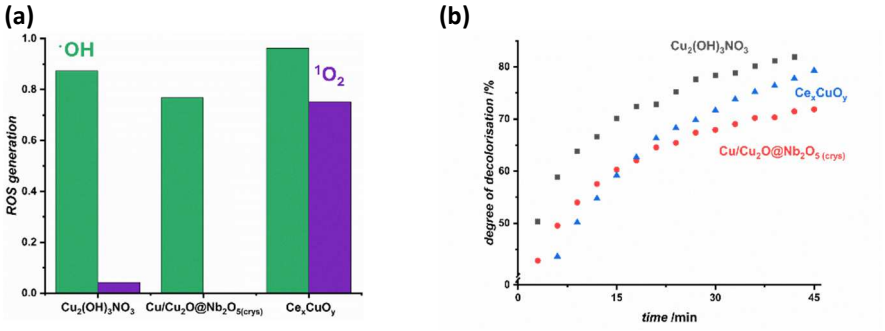


Figure 1 Comparison of the ability of the tested materials in a) generation of hydroxyl radicals (green) and singlet oxygen (purple), b) and in discoloration of Direct Blue 15.

References

1. B. Mozgawa, K. Sobańska, J. Gryboś, P. Pietrzyk, *Catalysis Today* **2022**, *384-386*, 156-165.

Acknowledgements

This work was financially supported by the National Science Center, Poland (NCN), grant OPUS27 2024/53/B/ST4/03929.

Esterification of hexanoic acid to hexyl hexanoate with heterogeneous acid catalysts: preliminary evaluations with Amberlyst and niobium- zirconium-phosphates

Anna Maria RASPOLLI GALLETTI *[,1], Leonardo CARMASSI [1], Nicola DI FIDIO [1], Sara FULIGNATI [1], Claudia ANTONETTI [1], Domenico LICURSI [1]
[1]*University of Pisa, Department of Chemistry & Industrial Chemistry, Via Giuseppe Moruzzi, 13, Pisa, Italy.*
** anna.maria.raspolli.galletti@unipi.it*

Significance and Relevance

Hexyl hexanoate (HexHex) is an ester of potentially relevant industrial interest, actually exploited as fragrance and lubricant, but also as an oxygenated additive for diesel fuels. It can be synthesised by esterification between hexanoic acid and 1-hexanol, a reaction occurring in the presence of an appropriate Brønsted acid catalyst. In this work, commercial heterogeneous Amberlyst resins and niobium- and zirconium-phosphates, have been tested for the synthesis of HexHex, optimized with the aim of reducing both the catalyst loading and the excess of the alcohol. After univariate screening of the reaction parameters, Amberlyst- A 35 was identified as the most interesting catalyst, identifying the best reaction conditions (catalyst loading: 0.5 wt%, temperature: 120°C, time: 8h, alcohol/acid molar ratio = 2), leading to a maximum hexanoic acid conversion of about 93 mol%, with a complete selectivity to the target ester. This promising achievement encourages further deepening of the kinetic aspects, to further improve its sustainable and clean production for energy uses.

(Preferred topic) Green chemistry and biomass transformation, renewable resources conversion; (2nd choice) Sustainable and clean energy production and transport
Preferred presentation: Only poster

Introduction and Motivations

Esters have great industrial interest, thanks to their various applications (solvents, flavours, lubricants, plasticisers, and biofuels). [1] The esterification reaction is an equilibrium reaction, needing of an appropriate Brønsted acid catalyst to overcome the kinetic issues. Moreover, an excess of the alcohol is generally employed (typically, alcohol/carboxylic acid molar ratio higher than 4), and the removal of the produced water is carried out to maximize its production. [2] In this wide scenario, HexHex is industrially attractive as fragrance and lubricant, but also potentially exploitable as oxygenated additive for diesel fuels. [1] As for other esters, sulfuric acid has been traditionally used to catalyse HexHex synthesis, but mineral acids lead to environmental corrosion and work-up issues. [3] For these reasons, in this work, as a part of PRIN 2022 REFIL, commercial acid resins (Amberlyst), and niobium or zirconium phosphates (NbPO and ZrPO, respectively), were tested for the HexHex production, aimed at improving the economy and the sustainability of this reaction. Further univariate optimization adopting the most performing Amberlyst- A 35 was carried out, reducing the catalyst loading at the best, keeping a low alcohol/carboxylic acid molar ratio (equal to 2). The obtained promising results encourage further deepening of the kinetic aspects of the HexHex synthesis, to further improve its sustainable and clean production for energy uses.

Materials and Methods

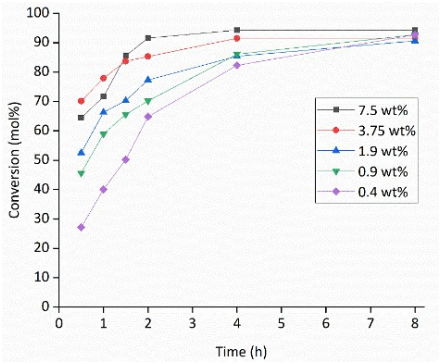
Esterification tests were carried out in a 160 mL pressure tube, which was loaded with the reagents and the catalyst (2 g of hexanoic acid, 3.5 g of 1-hexanol and the selected amount of catalyst). Afterwards, the pressure tube was sealed, placed in a thermostated oil-bath, and the reaction slurry was kept under magnetic constant stirring during the entire reaction. The analytical determinations were performed according to our previous work. [1]

Results and Discussion

Preliminary screening evaluations were carried out on the catalysts of interest, univariately changing the temperature (110-130 °C) and catalyst loading (12.0-0.4 wt%). The alcohol/acid molar

ratio was kept constant at 2, which represents a good improvement over the available state of the art. [2] First of all, Amberlyst-A 15 (8 wt%) was adopted as the starting acid resin, operating at a temperature of 110°C, achieving the hexanoic acid conversion of about 83 mol% after 2 h and about 89 mol% after 8 h, an achievement which represents a good starting point for further optimization. In an attempt of further improving the substrate conversion and considering the low thermal stability of the Amberlyst-A 15 (maximum operating temperature = 120 °C), the use of more thermally stable Amberlyst-A 35 was considered, working at a higher reaction temperature (120 °C), with the same acidity of the previous Amberlyst-A 15 catalyst (Amberlyst-A 15= 4.7 meq H^+/g_{resin}, Amberlyst-A 35= 5 meq H^+/g_{resin}). Further increase of the temperature from 110 to 120 °C only slightly increased the hexanoic acid conversion from 89 to 94 mol%, and further temperature increase up to 130 °C did not allow any further improvement of the conversion parameter. The effect of the Amberlyst acidity was evaluated, trying to significantly lower the catalyst loading (within the range 7.5-0.4 wt%, corresponding to 2.24-0.20 meq H^+ in the reaction mixture), keeping constant the reaction temperature at 120 °C (Figure 1). The reaction rate slowed down by progressively decreasing the catalyst loading, whereas the plateau of conversion (and yield) was always achieved after 8 h. After having minimized the catalyst loading at the best (0.2 wt%), working at 120 °C, niobium and zirconium phosphates (NbPO and ZrPO, respectively) were tested for the same purpose, exploiting their well-known acidic properties. [4] In this context, the acidity of NbPO and ZrPO was kept constant (0.2 meq H^+ in the reaction mixture), achieving similar conversion data (58 and 60 mol% respectively). Based on these preliminary results, Amberlyst-A 35 was identified as the best catalyst for HexHex production, which encourages further deepening of the kinetic aspects. Further insight about the cheapest and simplest way for entrapping/removing the water of reaction is in progress, before moving towards the conversion of real hexanoic acid-rich feedstocks obtainable from the chain-elongation fermentation of a wide variety of waste biomasses.

Figure 1 Kinetics data for the HexHex synthesis at 120 °C, employing progressively lower catalyst loadings of Amberlyst-A 35.



References

1. D. Licursi, A. M. Raspolli Galletti, C. Antonetti, G. A. Martinez, E. Jones, L. Bertin, N. Di Fidio, S. Fulignati, G. Pasini, S. Frigo, *Catalysts* **2022,** *12*, 1550
2. M. Kulawska, M. Organek, W. Organek, *International Journal of Organic Chemistry* **2017** *7* , 336-345
3. V. Russo, F. Taddeo, T. Cogliano, R. Vitiello, R. Esposito, R. Tesser, T. Salmi, M. Di Serio, *Chemical Engineering Journal* **2021**, *408*, 127238
4. C. Antonetti, A. M. Raspolli Galletti, D. Licursi, S. Fulignati, N. Di Fidio, F. Zanetti, A. Monti, T. Tabanelli, F. Cavani, *Catalysts* **2022**, *12*, 1189

Acknowledgements

The authors thank the PRIN 2022-Project REFIL "*Renewable liquid Fuel of new generation from wastewater sludge: a step towards circular economy*" (Progetti di Ricerca di Rilevante Interesse Nazionale – Bando 2022 - 2022KA5WL8).

Ibuprofen photodegradation under visible light promoted by Fe-doped nano CeO_2

Vincenzo RUSSO[*,1], Rosanna PAPARO[1], Olimpia TAMMARO[2], Martino DI SERIO[1], Serena ESPOSITO[2]
[1] *Università di Napoli 'Federico II', Department of Chemical Sciences, Napoli, Italy.*
[2] *Department of Applied Science and Technology and INSTM Unit of Torino – Politecnico, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy.*
* v.russo@unina.it

Significance and Relevance

The main novelty of the paper was the synthesis of an active catalyst for ibuprofen photodegradation under visible light irradiation. Reverse micelle synthesis fosters Fe doping of nanocrystalline CeO_2. From the synthesis, it was revealed that 2.5 mol % iron-doped ceria leads to high charge delocalization. Testing the synthesized catalysts, it was revealed that efficient visible-light photodegradation of ibuprofen was promoted using 2.5 mol % Fe-CeO_2. It was demonstrated that substitutional Fe favours the oxygen vacancies formation and ibuprofen adsorption.

Preferred and 2nd choice for the topic: Water treatment, Photocatalysis and photoelectrocatalytic approaches, solar energy utilization.
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Reverse micelle nanoreactors were successfully designed to synthesize small-sized ceria nanocrystals (3.5–4.2 nm) with a sizeable amount of substitutional iron. Undoped and doped CeO_2 catalysts with an iron content (0.50–10 mol %) compliant with the nominal value were prepared and tested for the first time for the removal of ibuprofen both in the dark and under UV or visible light irradiation. The effective inclusion and distribution of iron in the ceria lattice were ascertained through in-depth physicochemical characterization. In particular, X-ray diffraction suggested the formation of an F-type crystal structure, ruling out the formation of separate iron-containing crystalline phases. On the other hand, substitutional doping of CeO_2 with Fe atoms favoured the formation of Ce^{3+} defects and vacancy sites (VOs) with a maximum for the sample with 2.5 mol % iron (Fe2.5), as evidenced by X-ray photoelectron spectroscopy (XPS) measurements and Raman spectroscopy. UV–Vis spectroscopy showed that the optical properties were successfully modified by the presence of iron, which causes a gradual decrease in band gap as iron content increases. Nevertheless, it was found under dark conditions that adsorption capacity does not monotonically increase with iron content, revealing contrasting roles of surface characteristics. Indeed, catalytic experiments have identified a trade-off between adsorption and photodegradation, identifying Fe2.5 as the best-performing catalyst for ibuprofen removal under visible light irradiation. These results were discussed by considering the key properties of the catalysts as well as their different surface charge determined by ζ potential measurements. The best catalyst was tested through reuse experiments that proved its stability over 4 cycles.

Materials and Methods

In a typical synthesis, adapted from the literature[1], the oil/surfactant phase is prepared by dissolving 8.2 g of surfactant (Brij C10) in 100 mL of cyclohexane under stirring at room temperature. An aqueous solution is prepared by dissolving the proper amount of cerium and iron precursors in distillate water to achieve a final concentration of 0.5 M. The volume of the aqueous precursor solution has been selected to obtain a w0 value of 25 (w0 is defined as the water-surfactant molar ratio). The aqueous solution is slowly added dropwise to the oil phase to obtain appropriate water-in-oil (w/o) micelles. The optimized protocol involves alternating the additions of water and the co-surfactant. Finally, 5.4 mL of precipitating agent, ammonia solution, are slowly dripped. The mixture is stirred for 1.5 h at room temperature. The dried powder has been manually ground before being calcinated at

120 °C for 6 h. The amounts of cerium and iron were calculated to obtain a nominal composition expressed as a molar % of iron equal to 0 mol % (CeO_2), 0.5 mol % (Fe0.5), 2.5 mol % (Fe2.5), 5 mol% (Fe5) and 10 mol % (Fe10). The photodegradation experiments were conducted in a 1.5 L jacketed glass vessel, closed with a three-neck lid. The reactions were carried out using a co-axial lamp, connected to the reactor through the central neck of the lid. In particular, two different lamps were used: a lamp irradiating in the visible region (Sylvania T5, with a power of 4 W and a color temperature of 6500 K, solar emission spectrum, potential difference 220 V, and geometry 14 cm x 1.5 cm), or a lamp irradiating in the UV region (Toshiba FL4BLB, with a power of 4 W and emission at a wavelength of 365 nm, potential difference 220 V, and geometry 15 cm x 1.5 cm). ne neck of the lid was left free for collecting samples during the reaction, while the last neck is used for measuring the solution temperature through a dedicated thermocouple. The reaction temperature was controlled using an ultra-thermostat while the dispersion agitation was ensured by magnetic stirring. The airflow rate was set through an electronic gas flowmeter regulator (supplied by Bronkhorst).

Results and Discussion

Adsorption and photodegradation tests were conducted to investigate the performance of each synthesized catalyst. An attempt was made to justify the adsorption efficiency with the main properties of the catalysts. Except for the Fe10 sample, we do not observe any significant difference in terms of SSA and pore size. These findings lead us to speculate that the adsorption behaviour of IBU, except for Fe10, should not be determined by textural properties but could reflect differences in surface charge. For this reason, the ζ -potential values at the pH of ibuprofen solution (pH = 4.6), extrapolated from the ζ -potential curves, were plotted vs the maximum adsorption capacity (q_t=($C_{IBU,0}$-C_{IBU})/ρ_B), measured in dedicated experiments (Fig. 1A).

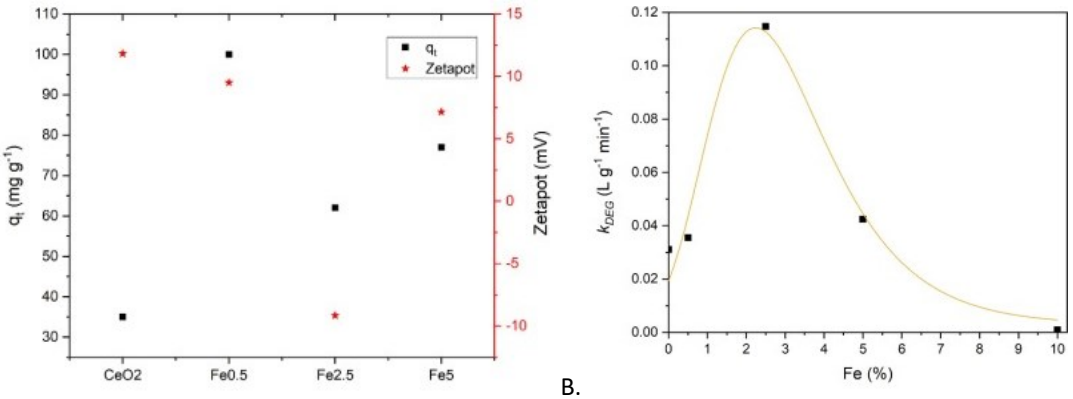


Figure 1 A. Potential (ζ) of the pristine and Fe-doped CeO_2 vs the adsorption capacity. b) Trend of the adsorption equilibrium constant. The present experimental conditions were adopted for each experiment: T = 30 °C, $C_{IBU,0}$ = 12.4 mg/L, ρ_B = 0.07 g/L, reaction time of 300 min. B. Plot of the degradation constant as a function of Fe loading.

The photodegradation experiments were conducted either in the presence of visible irradiation. The performance of the catalysts under visible irradiation is indeed promising for a scale-up process, considering the low lamp power and the used dosage of the catalysts. Fig. 1B clearly illustrates that Fe2.5 is the best performing photocatalyst as it shows the highest degradation constant.

In conclusion, meticulous synthesis strategies for the preparation of robust and efficient photocatalysts allowed an efficient removal of ibuprofen (an emerging contaminant) from waters, using visible light-activated photocatalytic processes.

References

1. O. Tammaro, R. Paparo, M. Chianese, I. Ritacco, L. Caporaso, M. Farnesi Camellone, B. Masenelli, A.D. Lamirand, J.-M. Bluet, M. Fontana, G. Pinto, A. Illiano, A. Amoresano, M. Di Serio, V. Russo, S. Esposito, *Chemical Engineering Journal* **2024**, *479*, 147909.

Mechanistic Study on Generation and Growth of Ash Particles from Lubricant Additives

Junya ONODA[1], Akira ODA[1], Atsushi SATSUMA[1]
[1]*Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan.*

Significance and Relevance

The generation and growth mechanism of ash particles from lubricant additives was investigated from a molecular and microscopic point of view. TG-DTA results clarified the stepwise decomposition of calcium sulfonate and magnesium sulfonate, while ZnDTP decomposition proceeds only in one step. Although pure calcium ash forms small ash particles with a relatively uniform size distribution, Zn-containing ash forms large sphere particles around 1000 nm because of the role of Zn as a binder of ash particles

Preferred for the topic: Automotive and stationary emission control, Air cleaning and combustion
Preferred presentation: Poster

Introduction

Clean diesel vehicles are equipped with a particulate filter (DPF: Diesel Particulate Filter). Accumulation of ash in the DPF is one of the serious problems,[1-3] therefore, the effects of ash accumulation have been investigated mainly on DPF pressure drop, pumping losses, and increase in regeneration frequency, and so on.[4-6] The present study focused on the chemistry of ash generation from additive molecules and the growth of ash particles.

Experimental

Calcium sulfonate (TBN=400), Magnesium sulfonate (TBN=400), and Zinc dialkyldithiophosphate (ZnDTP) were supplied as a diluted solution in a base oil. TG-DTA profiles were measured with Rigaku TG8121 thermogravimeter in a flow of 0-20% O_2/N_2 (100 mL min^{-1}) at a heating rate of 5 °C min^{-1}. To observe the particle growth of Ca-derived ash particles, a model PM (particulate matter) was prepared by impregnation of an aqueous solution of $(CH_3COO)_2Ca \cdot H_2O$ to model carbon (Printex V), followed by evaporation at 60 °C, dryness overnight at 80°C, and calcination in pure N_2 at 500°C for 3 h.

Results and Discussion

1. Decomposition of Oil Additives to Ash

Thermal decomposition of additives was evaluated by TG-DTA. As shown in Figure 1, the weight of the diluted calcium sulfonate decreased stepwise. The residual weight of zero means that the diluted additives are completely converted to inorganic ash such as $CaCO_3$ and $CaSO_4$. The oxygen concentration did not much affect the decomposition temperature. From the weight ratio and heat generation, the stepwise decomposition can be assigned to (1) partial oxidation and subsequent removal of the side chain around 300 °C, (2) oxidation or removal of aromatic rings at 400-500 °C, and (3) removal of SO_2 at 700-800°C (Figure 2). The rate of weight loss at 300-400°C was sensitive to both the oxygen concentration and temperature ramp rate, however, the inflection temperatures were not affected. Similar profiles were observed for the decomposition of magnesium sulfonate. As for ZnDTP, only a rapid weight loss at around 280 ˚C was observed.

2. Growth of Ash Particles

The states of residual components in an oxygen-containing atmosphere were analyzed by XRD and Raman. In Raman spectra, the G-band and D-band of soot derived from organic parts of additives were observed below 700 °C, and the bands disappeared after heating at 800 °C. The crystalline size of inorganic compounds was estimated from XRD patterns and shown in Figure 3 as a function of temperature. Only $CaCO_3$ was observed below 600 °C, while $CaSO_4$, and CaO were also formed above 600 °C, indicating decomposition of $CaCO_3$ into CaO and sulfation of $CaCO_3$ and/or CaO at higher temperatures. Although the crystalline size from XRD was below 40 nm, the particle size distribution of ash analyzed by Laser diffraction was around 200-1000 nm. The results mean that the ash particles are composed of agglomerated small primary ash particles to form secondary particles.

The state of the secondary particles was measured with STEM-EDX using the model PM ($CaCO_3$ supported on carbon black). After heat-treated at 700-900 °C in 10% O_2, agglomerated cubic crystals

of $CaCO_3$ were observed. Their sizes were in a relatively narrow range around 50 to 100 nm. When the model PM and a residual of heat-treated ZnDTP at 500 °C were mixed (Ca/Zn = 1:1) and heated at 700 °C for 3 h in 10% O_2, very large sphere particles around 1000 nm were observed. The chemical analysis by EDX revealed that Zn is concentrated in the sphere particles. Considering the low melting point of Zn metal at 419 °C, the role of Zn metal in the formation of the large sphere particles can be speculated.

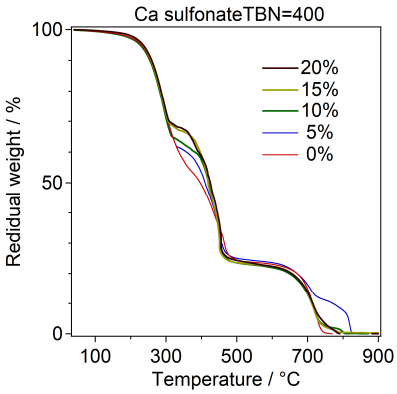


Figure 1. TG profiles of calcium sulfonate decomposition under various partial O_2 concentrations.

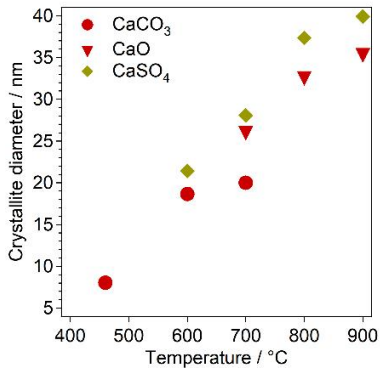


Figure 3. Temperature dependence of crystalline diameter of calcium sulfonate derived ash.

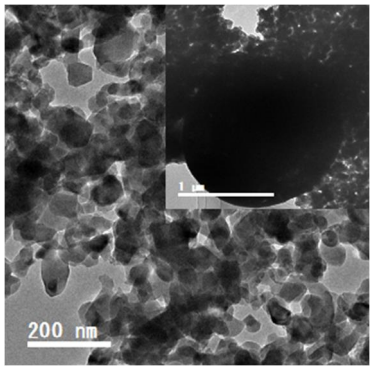


Figure 4. TEM images of ash derived from calcination of $CaCO_3$/C and ZnDTP mixture at 700 °C for 3 h.

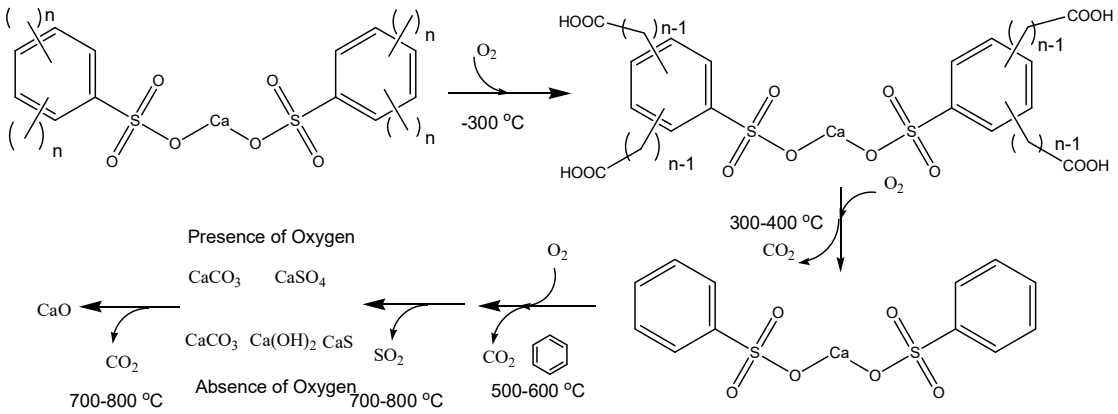


Figure 2. Schematic scheme of calcium sulfonate decomposition into ash.

References

1. A. Liati, et al., Atmos. Environ., 49 (2012) 391.
2. A. Liati, et al., J. Nanopart. Res., 14 (2012) 1224.
3. A. Liati, et al., Combust. Flame, 157 (2010) 1658.
4. A. Sappok, et al., SAE Int. J. Fuels Lubr., 3 (2010) 705.
5. J. Fang, et al., Appl. Thermal Eng., 124 (2017) 633.
6. Y. Liu, et al., SAE Int. J. Engines, 8 (2015) 1313.

Acknowledgments

This work is the result of the research project with The Research association of Automotive Internal Combustion Engines (AICE). The authors gratefully acknowledge the concerned personnel. The authors thank Dr. Yuta Yamamoto, Institute of Materials and Systems for Sustainability, Nagoya University, for their contribution to STEM-EDX measurements.

(Ni,Cu) catalysts for ethanol dehydrogenation: performances vs. synthesis

Elena Spennati[1,2], Giovanni Pampararo[3], Gabriella Garbarino[1,2], Paola Riani[2,3*]
[1] *University of Genova, DICCA Dept., Genova, 16145 (Italy)*
[2]INSTM, *UDR Genova, 16146 (Italy)*
[3] *University of Genova, DCCI Dept., Genova, 16146 (Italy*)
elena.spennati@edu.unige.it, *paola.riani@unige.it

Significance and Relevance

Renewable hydrogen as an energy vector will play a crucial role in the next future. In this work, hydrogen was produced as a by-product of the dehydrogenation reaction of bioethanol to acetaldehyde, an important chemical compound. The stability and activity of the Cu-based catalyst, the most investigated for this reaction, was significantly improved by a small amount of Ni addition at low temperatures, giving better results than the commercial catalyst.
This research provides fundamental understanding in the frame of renewable hydrogen production in the context of energy transition.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion, H_2 storage and transportation, green H_2 production, hydrogen vectors

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Considering the global environmental crisis, it is of paramount importance to identify and develop new, innovative, and environmentally friendly sources of energy[1]. Among the various potential energy carriers, hydrogen is a promising option. According to long-term forecasts (until 2050), H_2 will be a key player in the global economy, accounting for up to 20% of energy use[2]. The global demand for hydrogen is approximately 70 Mt_{H_2}/year, with current production exceeding 95% derived from fossil fuels[3]. Among the potential research path, the dehydrogenation of bioethanol to acetaldehyde is a promising avenue. In fact, bioethanol, produced by the fermentation of biomass, is expected to become a primary intermediate in the emerging industrial organic chemistry based on green chemicals. Among the studied active phases, Cu- has gained increasing interest due to its low cost and greater environmental compatibility than copper chromite catalysts, which are the conventional catalyst for this reaction. The main weakness is the rapid catalyst deactivation due to carbon deposition and metal sintering[4,5]. In the open literature, it has been demonstrated that the addition of Ni to nanoscale copper alloys enhances the stability and performance of the catalyst[6]. The objective of this study is to investigate the bioethanol dehydrogenation on (Cu,Ni) catalysts as a function of preparation and to study the interaction of reactants and adsorbed species-intermediates on the catalyst surface in operando condition by FT-IR.

Materials and Methods

The (Ni,Cu)/Al_2O_3 catalysts were prepared by hydrothermal treatment (HT) and optimized solid combustion synthesis (SCS), maintaining a total metal loading of 7.5 wt.%. The prepared catalysts were characterized by XRD, FE-SEM, FT-IR, UV-vis-NIR, and BET. The catalytic performances were carried out and compared to commercial Cu-based catalyst in a laboratory scale plant in a quartz fixed bed tubular reactor with 7.9 (v/v)% ethanol in the temperature range 423-773 K. The reactant products were analyzed by GC and GC-MS to evaluate bioethanol conversion and acetaldehyde yield and selectivity. Operando DRIFTS experiments are ongoing and are carried out by FT-IR spectrophotometer and Praying Mantis accessory and cell (Harrick).

Results and Discussion

Figure 1 shows the catalytic performances in the bio-ethanol dehydrogenation reaction (7.9% v/v) obtained with monometallic (Cu) and bimetallic (Cu,Ni) catalysts. The Cu-based catalyst, Cu (SCS), exhibited superior catalytic performance in terms of acetaldehyde production compared to the commercial catalyst at temperatures below 573 K. This behavior can be attributed to the homogeneous dispersion of Cu on the Al_2O_3 support. Furthermore, the bimetallic catalysts exhibited enhanced catalytic performance compared to the monometallic catalyst, indicating a synergistic effect between Ni and Cu, especially for the catalyst prepared by HT. At low temperatures, the (Cu,Ni) (HT) catalyst demonstrated remarkable activity (90% ethanol conversion and 71% acetaldehyde selectivity at 523 K), with an H_2 production of 0.40 mg/min.

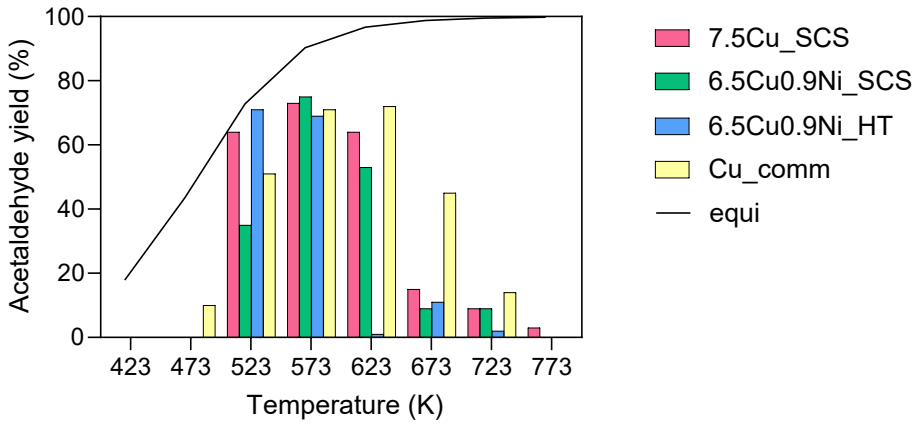


Figure 1. Catalytic performances obtained with the monometallic and bimetallic catalysts.

The catalysts pre-reduction resulted in enhanced catalytic performance at lower temperatures with both prepared bimetallic catalysts.

In conclusion, the addition of Ni to the Cu-based catalyst resulted in improved catalytic performance in terms of bio-ethanol conversion and acetaldehyde selectivity, in particular at low temperatures.

References

1. IEA.org/reports/CO_2-emissions-in-2022
2. IEA.org/reports/the-future-of-hydrogen.
3. Hydrogen4EU report. Charting Pathways to Enable Netzero. Deloitte Finance – IFPEN - SINTEF https://www.hydrogen4eu.com.
4. G. Pampararo, et al., Appl. Catal. A: General **2020**, 602, 117710
5. G. Pampararo, et al., Chemical Engineering Journal **2023**, 465, 142715
6. N. Janvelyan, et al., Catal. Sci. Technol. **2020**, 10, 5207-5217

Acknowledgements

G.G. and E.S. acknowledge the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3—Call for tender No. 1561 of 11.10.2022 of Ministero dell'Università e della Ricerca (MUR); funded by the European Union—NextGenerationEU project title "Network 4 Energy Sustainable Transition—NEST" (project code PE0000021).

Rare earth element modified nickel phosphide nanoparticles as electro- and photocatalysts for hydrogen generation reactions

Dorottya Szalay[1], Shik Chi Edman Tsang[1]*
[1] *Wolfson Catalysis Centre, Department of Chemistry, University of Oxford, Oxford, OX1 3QR, United Kingdom*
* edman.tsang@chem.ox.ac.uk

Introduction

With the rising global energy demand and urgent environmental issues, sustainable and renewable energy sources are essential to replace fossil fuels. Hydrogen fuel stands out due to its eco-friendliness and high energy output through combustion.[1] Hydrogen production via hydrogen evolution reaction (HER) can be achieved through electrocatalysis or photocatalysis. Platinum group metals (PGMs) are highly effective HER electrocatalysts, but their scarcity and high cost limit their practicality.[2] Recently, transition metal phosphides (TMPs) -such as nickel phosphide - have emerged as promising catalyst candidates due to their excellent stability under various conditions and ability to perform reversible association or dissociation of H to H_2.[3]

This work investigates the use of lanthanide ion-modified nickel phosphide (NiP) nanoparticles as highly efficient catalysts for hydrogen generation reactions: both electrochemical and photochemical HER. This class of materials displayed tunable electronic properties for optimized catalytic activities.

Materials and Methods

Pristine and various lanthanide-modified nickel phosphide nanoparticles (denoted as Ln-Ni_2P) were synthesized through a facile wet-chemistry method using a high-precision heating mantle and inert atmosphere. The resulting nanoparticles were characterized by PXRD, XPS, UPS and TEM. Particles were dropcasted onto carbon paper for alkaline electrochemical HER tests. Dye-sensitized photochemical HER was carried out using eosin Y dye and triethanolamine as sacrificial agent.

Results and Discussion

Electrochemical activities of the nanoparticles were evaluated using linear sweep voltammetry (LSVs) and results are shown on Figure 1. While all of them showed activity towards HER, incorporation of lanthanides did not improve catalytic activities. All catalysts showed relatively higher Tafel slopes, suggesting that the rate-determining step is associated with the Volmer step of HER, which involves the adsorption of hydrogen onto the catalyst surface.

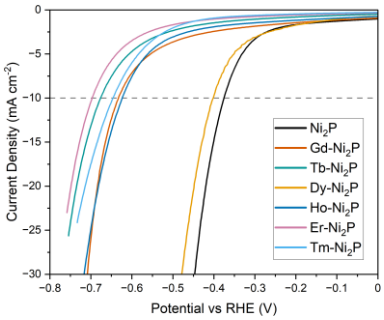


Figure 1. LSV of pristine and lanthanide modified NiPs in alkaline HER.

Ultraviolet photoelectron spectroscopy (UPS) was used to establish the metallic properties of all materials. The lack of band gap in these catalysts means they cannot be utilized in conventional colloidal semiconductor systems. However, their ability to act as cathodes in hydrogen reduction allows them to be used in efficient dye-sensitized photochemical HER in the presence of a sacrificial agent. Here, the only requirement of the catalyst is the ability carry out HER. This mechanism is illustrated on Figure 2b and involves 4 key steps: 1) excitation of electron from HOMO to LUMO of dye, 2) electron transfer, 3) production of H_2 and 4) electron transfer from sacrificial agent to dye. An interesting reverse-Vulcanic relationship was observed in the lanthanide series

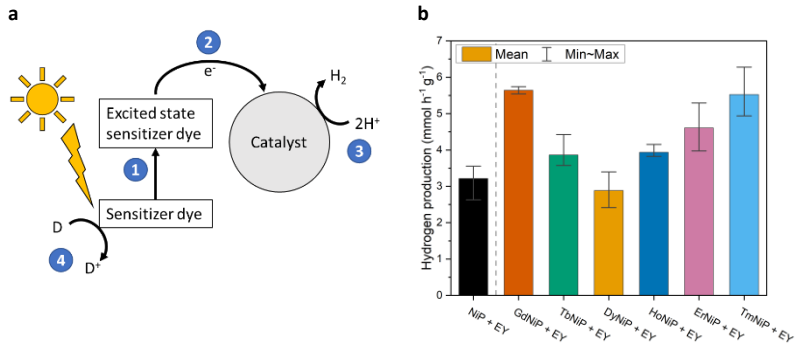


Figure 2. a) . Proposed mechanism scheme of dye-sensitized photochemical HER. b) Photocatalytic activity of pristine and Ln-Ni_2P.

Significance

Despite their misleading name, rare-earth elements are quite abundant. Replacing the currently used platinum group metals - that are expensive and are at risk of depletion - in hydrogen generation reactions would be an important step towards more efficient production of clean hydrogen energy at an industrial level. It is demonstrated the incorporation of small amounts of rare-earth elements into transition metal phosphides can alter catalytic permormances.

References

1. K. Mazloomi and C. Gomes, Renewable Sustainable Energy Rev., **2012**, *16*, 3024-3033.
2. C. G. Morales-Guio, L-A. Stern and X. Hu, Chem. Soc. Rev., **2014**, *43*, 6555-6569
3. H-W. Man, C-S. Tsang, M M-J Li, J. Mo, B. Huang, L. Y. S. Lee, Y-C. Leung, K-Y Wong and S. C. E Tsang, Appl. Catal., B, **2019**, *242*, 186-193

In-situ XAFS Analysis on Redox Dynamics of Precious Metal-supported Ce Complex Oxides

Hidetaka Tanabe[1], Daiju Matsumura[3], Shinya Uegaki[2], Shota Hamada[2], Takehisa Oseki[4], Tomohisa Mizuno[4], Shunsuke Oishi[4], Masami Nakamoto[5], Tetsurou Oonishi[5], Kazuya Yasuda[5], Hirohisa Tanaka[2, *]

[1]*Kwansei Gakuin University, Program of Materials Science, Sanda, Hyogo Japan.*

[2]*Kwansei Gakuin University, Graduate School of Science and Technology, Sanda, Hyogo Japan.*

[3] *Japan Atomic Energy Agency, SPring-8, 1-1-1 Koto Sayo, Sayo, Hyogo, Japan.*

[4]*Cataler Corporation, 1905-10 Shimonobe, Iwata, Shizuoka, Japan.*

[5]*Daihatsu Motor Co., Ltd., 2-1-1 Momozono, Ikeda, Osaka, Japan.*

** e-mail corresponding: hirohisa.tanaka@kwansei.ac.jp*

Significance and Relevance

In-situ XAFS studies on the fine structure and oxygen storage dynamics of CeO_2-based complex oxides with precious metals were performed at the BL14B1 and BL14B2 beamlines at SPring-8. H_2 and CO were used as reducing gases, and their differences were analyzed. The results showed no change in the fine structure of Ce and near elements after reduction by either gas, though CeO_2 was reduced faster by H_2 than CO. These results indicated the need for evaluation using real vehicle model gases due to differences in reduction rates and the many species of emissions gases in real vehicle environments[1][2].

Introduction and Motivations

The automotive industry has reached a turning point, and emissions regulations for internal combustion engine vehicles are being further tightened. In Europe, On-Board Monitoring (OBM) regulations are scheduled to be introduced in EURO7 from 2025 onward, creating an immediate need for technological innovation in internal combustion engine vehicles. In particular, On-Board Diagnostics (OBD) standards will be tightened, requiring precise management of the deterioration of the Oxygen Storage and release Capacity (OSC) of precious metal-loaded ceria-based complex oxides.

Materials and Methods

In this study, oxygen storage and release dynamics and the fine structure of CeO_2-based complex oxide with Pd were analyzed by Conventional and Dispersive XAFS at Ce *K-edge* in BL14B1 and BL14B2, SPring-8[3][4].

Table 1. Percentage of sample contained in the sample

Sample	Oxide weight ratio			Composition (Atomic ratio)
	CeO_2	ZrO_2	Y_2O_3	
Pd(0.5 wt%)/CZY40	40	55	5	$Ce_{0.32}Zr_{0.62}Y_{0.06}O_{2-\delta}$

Samples were heat treated at high temperatures to reproduce the degraded catalyst. This method allowed us to evaluate the robustness of the catalysts and the dynamics of the OSC as actually degraded. *In-situ* EXAFS and Dispersive XAFS measurements were carried out at Ce *K-edge* (40,443 eV) using the high energy of SPring-8. White X-rays dispersed by Si (311) curved crystals were incident on the sample, and the X-ray intensities before and after transmission were measured by an ion chamber. *K-edges* of Pd, Zr, and Y were measured by the transmission method. All samples were pretreated for oxidation. O_2 20% (N_2 balance) was used as the oxidizing gas. H_2 5% (N_2 balance) or CO 10% (N_2 balance) was used as the reducing gas. During the measurement, the oxidizing and reducing gases were alternately flowed at 400 °C.

Results and Discussion

DXAFS analysis showed that H_2 reduction proceeded faster than CO until 40 to 50 seconds. However, the reduction rate decreased after that, and the final reduction reached at 100 s was found to be similar for both gases (Fig. 1).

On the other hand, the reduction rate by CO showed a steady rate until the switch to the oxidation process. No difference in oxidation rate was observed between H_2 and CO. These results indicate that there is a clear difference in the reduction rates depending on the species of reducing gases, and provide important knowledge in the reactivity of the catalysts.

Furthermore, the structural changes of Ce crystals during the transition from the oxidation state to the reduction state were investigated by Conventional XAFS using the same sample (Fig. 2) [5].

As a result, a decrease in the Ce-Ce bond distance (about 3 Å), a shift of the peak position to the left, and a decrease in the Ce-O bond (about 1.6 Å) were observed during the transition from the oxidation state to the reduction state.

This suggests that CeO_2 releases oxygen between Ce and Ce during the reduction process, which shortens the Ce-Ce bond distance. These results observed the difference in the reaction rate depending on the species of reducing gas, but also observed that there is no clear difference in the structural change of CeO_2.

The results of this research are expected to provide new knowledge on the mechanisms of reaction rates and fine structure of Ce and near elements changes with reducing gas species and contribute to the development of catalyst design for refined redox characteristics.

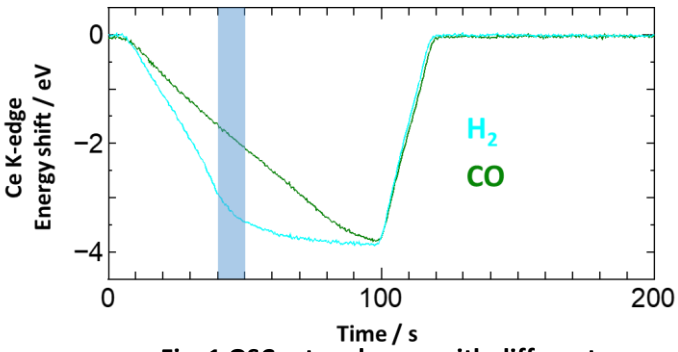


Fig. 1 OSC rates change with different reducing gas species

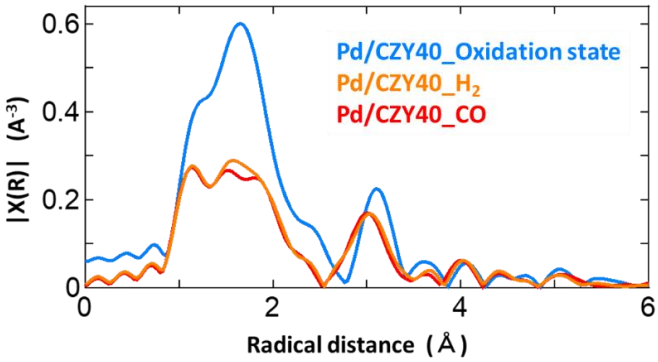


Fig.2 Ce and near elements fine structure of different reducing gas species

References

1. H. Tanaka, M. Yamamoto, 1996, Improvement in oxygen storage capacity, 231-238.
2. K. Yamada, H. Tanaka, M. Yamamoto, 1997, Oxygen storage capacity on cerium oxide-precious metal system, 1-8.
3. D. Matsumura, Y. Nishihata, J. Mizuki, et al. 2010, Dynamic structural change in Pd-perovskite automotive catalyst studied by time-resolved dispersive x-ray absorption fine structure.
4. Y.Nagai, T. Yamamoto, T.Tanaka, S. Yoshida, T.Nonaka, T. Okamoto, A. Suda, M. Sugiura, 2002, X-ray absorption fine structure analysis of local structure of CeO_2-ZrO_2 mixed oxides with the same composition ratio (Ce/Zr=1), 225-234.
5. Y. Nagai, T. Yamamoto, T. Tanaka, S. Yoshida, T. Nonaka, T. Okamoto, A. Suda, M. Sugiura, 2007, XAFS and XRD Analysis of Ceria–Zirconia Oxygen Storage Promoters for Automotive Catalysts.

Acknowledgements

The synchrotron radiation experiments were performed at SPring-8 beamlines BL14B1 and BL14B2 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal Nos. 2023B3618, 2024A3618 and 2024B1634). A part of this work was supported by the Advanced Research Infrastructure for Materials and Nanotechnology in Japan (ARIM Japan) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan (Grant Nos. JPMXP1223AE0021 and JPMXP1224AE0003) and the Shared-Use Program of JAEA Facilities (Proposal Nos. 2023B-E04 and 2024A-E06).

MW-assisted Pt@C_3N_4/TiO_2 composites for glycerol photoreforming for H_2 production

M.C. HERRERA-BEURNIO[1], C. ALIOTTA[2], F.J. LÓPEZ-TENLLADO[1], M. RUSSO[2], F. J. URBANO[1], A. MARINAS[1], M. L. TESTA[2] *

[1] *Departamento de Química Orgánica, Instituto Químico para la Energía y el Medioambiente (IQUEMA), Universidad de Córdoba, E-14071 Córdoba, Spain*

[2] *Istituto per lo Studio dei Materiali Nanostrutturati, Consiglio Nazionale delle Ricerche (ISMN-CNR), Via Ugo La Malfa 153, I-90146, Palermo, Italy*

** marialuisa.testa@cnr.it*

Significance and Relevance

Nowadays, hydrogen is considered as one of the most promising energy carriers and studies for green production are increasing in scientific literature. Glycerol photoreforming represents one of the greenest methods to produce hydrogen due to the use of both, a photocatalytic method, and glycerol as biomass-derived material. As known, TiO_2 is the most widely used photocatalyst, and to improve its use under visible light C_3N_4/TiO_2 composites are studied by using a MW-assisted procedure. The effectiveness of the MW is evident not only for its low-energy impact methodology but also for its effect on the morphology of the synthetized materials.

Preferred and 2nd choice for the topic: 1) H_2 storage and transportation, green H_2 production, hydrogen vectors, 2) Photocatalysis and photoelectrocatalytic approaches, solar energy utilization

Preferred presentation: Poster /Short Oral

Introduction and Motivations

Hydrogen and its generation through renewable raw materials are at the heart of the energy transition. Nowadays, hydrogen is often produced by using fossil fuels as starting materials. For this reason, the development of sustainable processes is an increasingly priority goal. In this context, glycerol photo-reforming for hydrogen production represents one of the greenest methods.[1] In fact, glycerol is, a biomass-derived material and photocatalysis is considered one of the most attractive ways to convert solar energy into usable chemicals. TiO_2 is, nowadays, the most used photocatalyst due to its efficiency, safety and affordability. Its principal drawbacks are its limited absorption to UV radiation and fast electron-hole pair recombination. C_3N_4 is a semiconductor that presents a narrower bandgap (2.7-2.8eV) than TiO_2 (3.2eV) so the corresponding C_3N_4/TiO_2 composites are able to extend the absorption to the visible light range. In a previous paper, the composites were produced in two different steps forming C_3N_4 on commercial TiO_2 P25. Here, with the aim to optimize and to make the process more sustainable, one-pot MW-assisted procedure is studied. C_3N_4/TiO_2 composites were thus prepared in only one step from melamine and Ti(iOPr)$_4$ precursor. The effectiveness of the MW is evident not only for its low-energy impact methodology but also for its effect in the morphology of the synthetized materials. Finally, Pt was deposited and tested as Pt@C_3N_4/TiO_2 composites for hydrogen photoproduction through glycerol photoreforming.

Materials and Methods

Here, an example of the synthesis of MW-assisted Pt@C_3N_4/TiO_2 materials is reported.

To obtain the heterojunction between titania and carbon nitride, melamine was dissolved in distilled water prior to adding titanium (IV) isopropoxide dropwise. The amounts were chosen to have a melamine: titania (w/w) ratio of 5. According to the MW-assisted procedure the solution was introduced in a microwave at 180 W for 20 cycles (on for 15 s and off for 20 s). Finally, the solid was filtered, washed with distilled water and dried. The solid was calcined at 550 °C for 1 h in a semi-closed system and denoted as MW_TiO_2CN. Pt@C_3N_4/TiO_2 was prepared by wetness impregnation. Briefly,

the appropriate amount of $PtCl_2$ so as to incorporate 1 wt.% of platinum was added to 0.5 g of each catalyst and the solid was calcined at 350 °C for 3 h.

Results and Discussion

Different titania-based photocatalysts were prepared by conventional or MW-assisted methodology[2-3] and compared as catalysts for hydrogen production through glycerol photoreforming. Carbon nitride was added, already prepared or in a one-pot procedure to improve the use of these systems under visible light. According to the design of this study, it is possible to compare the synthetic procedure (conventional/MW), if it has been carried out as a one-pot procedure or in two steps, and the influence of C_3N_4 in the systems. In all cases, Pt was impregnated onto the solids. All materials were well characterized by means of XRD, ICP-MS, N_2 adsorption-desorption, TGA/DSC, XPS, IR, and UV-Vis spectroscopy. From preliminary tests, microwave-synthesized solids show a lower bandgap value than conventional ones, which could improve their photocatalytic efficiency under visible light. Moreover, the influence of the microwave-assisted procedure seems evident also in hydrogen production and the results can be ascribed to the different crystallinity and surface area of MW materials.

References

1. M. C. Herrera-Beurnio, F. J. Lopez-Tenllado, J. Hidalgo-Carrillo, J. Martín-Gomez, R. Estevez, F.J. Urbano, A. Marinas, *Catalysis Today*, **2024**, 430, 114548 https://doi.org/10.1016/j.cattod.2024.114548
2. M. Russo, V. La Parola, G. Pantaleo, M. L. Testa, A.M. Venezia, R. Gupta, A. Bordoloi, R. Bal *Applied Catalysis A: General*, **2020,** 600, 117621
3. G. Gautier di Confiengo, M. G. Faga, V. La Parola, G. Magnacca, M. C. Paganini, M. L. Testa *Materials Chemistry and Physics*, **2024**, 321, 129485, https://doi.org/10.1016/j.matchemphys.2024.129485

Acknowledgements

The authors are grateful to MICINN for the projects PID2019-104953RB-I00/AEI/10.13039/501100011033 and PID2022-142275OB-I00/ AEI/10.13039/501100011033 and FEDER funds.

CO_2 methanation on the Ni-Mn-modified mesoporous silica

Margarita Popova*[,1,2], Grigoria Teohari [1], Gloria Issa[1], Daniela Kovacheva[3], Martin Kormunda[4]
[1] *Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, acad. G. Bonchev str., bl. 9, Sofia, Bulgaria*
[2] *National Centre of Excellence Mechatronics and Clean Technologies, Bulgaria*
[3] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, acad. G. Bonchev str., bl. 11, Sofia, Bulgaria*
[4] *Faculty of Science, University of Jan Evangelista Purkyně, Pasteurova 3632/15, 400 96 Ústí nad Labem, Czech Republic*
** Margarita.Popova@orgchm.bas.bg*

Significance and Relevance

The mesoporous silica was synthesized by a simple procedure from rice husks without template. Incipient wetness impregnation method was used for preparation of Ni-Mn-containing mesoporous silica catalysts. The strong influence of the Ni and Mn content and the peculiar properties of the applied mesoporous carrier on the formation of nickel and manganese oxide species with fine dispersion were demonstrated. Among the prepared catalysts, the 7 wt. % Ni- 3 wt. %Mn supported mesoporous silica catalysts showed the highest catalytic activity in CO_2 hydrogenation to methane. The activity and selectivity of the latter sample was kept for 5 hours reaction time.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling/ Air cleaning and combustion
Preferred presentation: poster/short oral

Introduction and Motivations

The increasing emission of greenhouse gases and their severe effect on the climate has come into the spotlight as a major challenge to sustainable development [1]. The European Green Deal is a new EU strategy aiming to combat climate change by no net emissions of (GHGs) by 2050. CCU is one of the most widely researched approaches, using CO_2 as an alternative, non-petrochemical precursor to chemical feedstocks. There is a broad spectrum of products, but the most valuable intermediates are synthesis gas, that can be used directly to produce fuels, and C1 compounds such as methanol, formic acid and methane [1]. The development of efficient catalysts is of key importance for the processes for CO2 valorization. The application of transition metal-containing (Ni, Co, Cu, Fe) catalysts is a good alternative of noble metals due to their affordable prices and high activity. However, the following order of activity was established. The catalytic support also influences the efficiency of the methanation process. The most promising supports are Al_2O_3, ZrO_2, CeO_2, MCM-41, SBA-15, and zeolites. A disadvantage of these materials is their high cost, which is due to the use of expensive reagents, incl. template, high temperature and longer procedure leading to higher energy consumption. A significantly more economical approach is the use of waste materials, low temperature and absence of expensive templates to obtain mesoporous silicas. Examples of raw materials for obtaining porous materials are most often agricultural waste, such as rice husks, etc.

In the present study, we have developed Ni-Mn- based mesoporous silica (MS) catalysts with high activity and selectivity for CO_2 conversion to methane.

Materials and Methods

The initial and modified materials were characterized by XRD (Bruker AXS Advanced X-ray Solutions GmbH, Karlsruhe, Germany), N_2 physisorption (Quantachrome instruments AUTOSORB iQ-MP-AG, Boynton Beach, FL 33426, USA), thermal analysis (STA449F5 Jupiter of NETZSCH Gerätebau GmbH (Netzsch, Germany), and solid-state NMR (Bruker Avance II+ 600 NMR spectrometer (Karlsruhe, Germany).

Samples were reduced in hydrogen (60 mL/min) up to 400 °C for 1h ex situ before the catalytic experiments. Hydrogenation of methane was performed at atmospheric pressure using a fixed-bed flow reactor. The amount of the catalyst which is used in the catalytic experiment is a 150 mg sample

with particle size 0.2–0.8 mm. The CO_2 reactant was fed in the reactor with a flow rate of 30 ml/min H_2 and CO_2, GHSV= 12 000 $cm^3h^{-1}gcat^{-1}$, (H_2/CO_2 is 4/1) and catalytic experiments were carried out in the interval 250–400 °C. On-line analysis of the reaction products was performed using a NEXIS GC-2030 ATF with a VALCO Plot VPHS-D CFS-PD3053-200 (30 m × 0.53 mm × 20.0 µm) column.

Results and Discussion

The XRD patterns of the reduced catalysts show the formation of finely dispersed nickel nanoparticles. Impregnation with nickel and manganese resulted in a decrease of the surface area but the shape of the isotherms is similar to the parent silica. Therefore, the changes are due to the pore blocking effect of incorporated metal oxides and metal oxide deposition on the outer surface.

Catalytic activity of the obtained catalysts in CO_2 methanation reaction was studied with increasing reaction temperature (Figure 1).

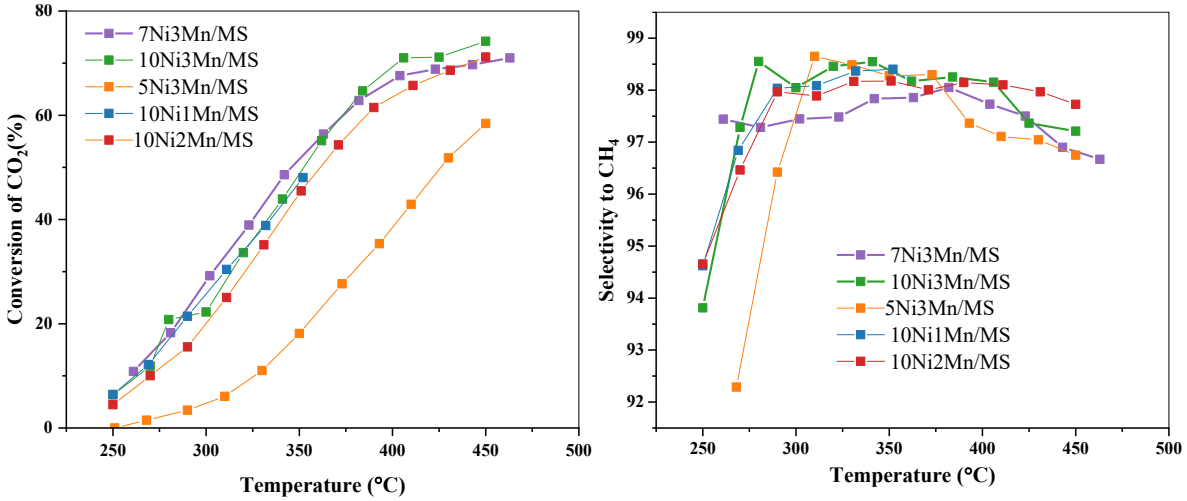


Figure 1. Catalytic activity of the studied catalysts as a function of reaction temperature (H_2:CO_2 = 4:1; GHSV = 12 000 mL $gcat^{-1}$ h^{-1}).

The highest catalytic activity and selectivity to methane were detected for 7Ni3Mn/MS catalyst. The presence of manganese facilitated the reduction of nickel during the reductive pretreatment and improved the nickel dispersion. Formation of Mn_xO_y has a positive effect on the catalytic performance because of the formation of basic sites with moderate strengths, enhancing the adsorption of slightly acidic CO_2. The basic sites promote the formation of monodentate formate species, that can be easily converted to methane. It was found that the presence of nickel nanoparticles and Mn_xO_y with the optimal ratio could result in higher activity and stability of the catalyst. Our results suggest that addition of manganese, a cheap and abundant transition metal, holds significant potential for industrial application in sustainable power to gas technologies.

References

1. P. Frontera, A. Macario, M. Ferraro, P. Antonucci, Catalysts, **2017**, 7, 59.
2. M. Popova, V. Mitova, M. Dimitrov, C. Rosmini, I. Tsacheva, P. Shestakova, D. Karashanova, I. Karadjova, N. Koseva, *Molecules*, **2024**, *29*, 3540.

Acknowledgements

The authors thank the European Regional Development Fund under "Research Innovation and Digitization for Smart Transformation" program 2021-2027 under the Project BG16RFPR002-1.014-0006 "National Centre of Excellence Mechatronics and Clean Technologies" for the financial support.

Oxide and zeolitic systems of catalytic importance synthesized from fly ashes from industrial energy sector

Paweł RYBOWICZ[1], Rafał PANEK[2], Artur ŁAGOSZ[3], Barbara GIL[1], Wiesław ROTH[1], Wojciech FRANUS[2], Andrzej ADAMSKI[*,1]

[1]*Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, 30-687 Kraków, Poland.*

[2]*Lublin University of Technology, Faculty of Civil Engineering and Architecture, Nadbystrzycka 40, 20-618 Lublin, Poland.*

[3]*AGH - University of Science and Technology, Faculty of Material Science and Ceramics, Mickiewicza Ave. 30, 30-059 Kraków, Poland.*

** a.adamski@uj.edu.pl*

Significance and Relevance

For many decades the conventional energy sector operating worldwide on fossil fuels and biomass to generate energy produces fly ashes (FAs) on a massive scale. One of the most ambitious ways to efficiently manage various FAs, remaining in accordance with principles of circular economy, is their use as anthropogenic raw materials to obtain functional systems such as catalysts, supports, or sorbents. In this work we present how to apply FAs to synthesize oxide phases, active in environmentally relevant reactions, catalytic supports for metals and oxides, or 3D and 2D zeolites. The latter group is particularly interesting from a catalytic viewpoint.

Preferred and 2nd choice for the topic:
Circular economy; Sustainable and clean energy production and transport;
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster) Oral preferred or Short Oral

Introduction and Motivations

Due to the diverse composition of the starting fly ashes, obtaining the appropriate structures of the functional materials suitable for catalytic applications is quite challenging. Each synthesis must be preceded by a thorough analysis of parameters characterizing the FAs, such as e.g.: the Si/Al element content ratio, the presence of iron and carbon residues, as well as the mineral and phase compositions. Also, the ratio of the glassy to crystalline phases has to be taken into consideration. Generally, FAs are characterized by relatively high contents of silicon and aluminum. These elements occur in ashes mainly in the form of aluminosilicate glaze, which is a typical building material of spherical grains called cenospheres. Such components can also exist in crystalline form as quartz and mullite. Catalytically useful oxide phases can be extracted from FAs generated from heavy oil combustion. Cenospheres without any specific treatment or after functionalization with transition metals can be used as catalytic supports or even as catalytically active composites. While the synthesis of zeolites with 3D structures from fly ashes is relatively well mastered, obtaining layered systems (2D), with active centers located close to the external surfaces, attractive from the catalytic point of view, also accessible to more spatially demanding molecules, is much more difficult. One of our main goals was to check the possibility of synthesizing layered zeolite structures and to indicate the parameters controlling their type. Obtaining the functional, catalytically useful structures is a significant step towards both efficient fly ash valorization and more sustainable synthesis of an impressive variety of advanced materials.

Materials and Methods

FAs obtained from industrial power plants have been investigated to be applied as precursors for synthesis of catalytic materials mentioned above. All ashes were generated by coal combustion in pulverized-fuel boilers. Additionally, one type of ash generated from heavy oil combustion has also been investigated. Bare oxides, supported oxide systems containing both supports and active phases prepared from fly ashes as well as NaX, MCM-22 and 2D zeolites were synthesized by optimized wet chemistry procedures. Both FAs used for syntheses and the obtained new materials have been in-depth characterized by XRF, XRD, RS, BET, SEM, DRIFT and UV/Vis-DR techniques.

Results and Discussion

As an initial scientific task, key parameters of fly ashes, determining their possible catalytic applications were selected and analyzed in detail [1]. Structural, textural and functional characterization of FAs, chosen as starting materials, promising for synthesis of both oxide systems and zeolites, has been performed with particular attention paid to those features, which can be decisive for preparation of different classes of catalytic materials [2]. The synthetic impact of such parameters as the presence of residual carbonaceous impurities, the content ratios of the glass to crystalline phases or Si to Al have been elucidated and better understood. Moreover, the importance of such textural properties as specific surface areas, particle types and their size distributions have been analyzed in detail. Fly ashes are rich in silicon, aluminum and sometimes also in iron or titanium. Due to their attractive composition, high availability, and relatively low prices, FAs were satisfactorily tested as substrates e.g., for synthesis of NaX zeolites (3D), MCM-22P systems (being precursors of 2D zeolites of MCM-56 type) (see Fig.), as well as of the layered (2D) bifer zeolite structures [3]. Another option, practically verified in our studies, can be the oriented synthesis of heterogeneous oxide catalysts. Especially, the FAs from the combustion of heavy oil fractions, rich in such transition elements as V and Mo, are particularly attractive as precursors of catalytically active phases active in redox reaction of environmental importance. The obtained results clearly confirmed both the complex nature of the fly ashes and their evident potential to be used for synthesis of advanced materials mentioned above. In turn, bare and functionalized cenospheres have been applied as supports for copper and zinc, and tested in such environmentally sound reactions as SCR NO_x and CO_2 hydrogenation to methanol. The presented sustainable pro-ecological approach to FA valorization remains in agreement with principles of circular economy and permits to exploit high potential of fly ashes as anthropogenic raw materials of catalytic relevance.

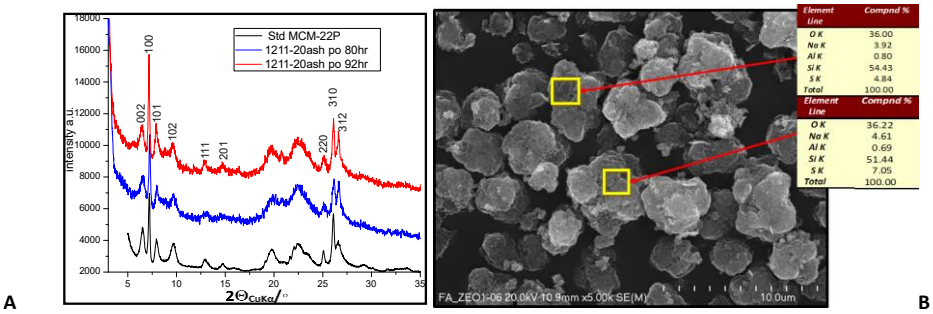


Figure. Structure (A) and morphology (B) of MCM-22 materials synthesized from fly ashes together with chemical composition of the selected region determined by EDX.

References

1. P. Rybowicz et al., *Energy Fuels.* **2020**, *34*, 6229
2. P. Rybowicz et al., *Sust. Chem. Pharm.* **2022**, *13*, 100637
3. W.J. Roth et al., *JACS*, **2021**, *143*, 11052

Acknowledgements

The research has been supported by a grant from the Priority Research Area Anthropocene (FP Man-Mind-Environment Hub) under the Strategic Programme Excellence Initiative at the Jagiellonian University. Contribution of P.R. to this work was also supported in the framework of POWR.03.02.00-00I004/16 and of Talent Management POB Anthropocene grants.

Simultaneous waste remediation and carbon capture via CO_2 mineralization over industrial basic wastes

Alessandro ALLEGRI[1], Valentina SCOGNAMIGLIO[2], Maria Chiara BIGNOZZI[2,3], Alessandro DAL POZZO[3], Alberto Renato DE ANGELIS[4], Roberto MILLINI[4], Stefania ALBONETTI[*,1]

[1] *University of Bologna, Department of Industrial Chemistry "Toso Montanari", C3 – Center for Chemical Catalysis, CIRI-FRAME, Via P. Gobetti 85, Bologna, Italy.*

[2] *Centro Ceramico, Via Valle d'Aosta, 1, Sassuolo, MO, Italy*

[3] *University of Bologna, Department of Civil, Chemical,– DICAM, via U. Terracini 28, Bologna, Italy.*

[4] *ENI S.p.A. Research and Technological Innovation Department, Via F. Maritano 26, San Donato Milanese, Italy*

** stefania.albonetti@unibo.it*

Significance and Relevance

Carbon capture is a mature technology and is necessary to dampen the impact of our industrial landscape and help bridge the gap between it and a renewable resources-based one. Despite this, its adoption has been slow due to its costs and the lack of incentives. In this work, a novel approach to capturing CO_2 using Air Pollution Control (APC) residues from the ceramic industry plants is presented. This approach not only is capable of reducing carbon emissions but also avoid a hazardous waste stream that would otherwise have to be disposed of.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling, Circular economy

Preferred presentation: Oral preferred

Introduction and Motivations

One of the main challenges in the adoption of carbon capture technologies on a large scale is the lack of incentives compared to its high cost. Amines scrubbing – the prevalent technology in the field – is costly, both to install the necessary plant and to operate it, due to its high energy cost and the degradation of the amine sorbent. This has left a wide margin for the development of competing technologies.[1] One example of this is mineral carbonation: this approach to carbon capture aims to promote and accelerate the natural weathering of calcium and magnesium-based silicates to produce the corresponding carbonates (along with silica) [2]. Among the challenges of this approach are the low reactivity of the materials, which only undergo spontaneous carbonation over millennia, and the logistics of the process. In particular, these minerals have to be mined, crushed to a powder and transported to the carbonation site. After carbonation, the resulting materials are often used as backfill in the mine, which is yet another logistics cost.

The proposed approach instead aims to take advantage of the existing industrial landscape, using readily available industrial wastes to capture CO_2 [3]. Due to the widespread application of hydrated lime in the abatement of acid flue gases, several industrial sectors produce **spent lime (SL) as waste**. Spent lime is often disposed of while still far from completely spent due to safety concerns and is classified as hazardous waste by European legislation. Its application as a CO_2 sorbent would simultaneously decrease the CO_2 emissions and the SL disposal costs. For SLs coming from ceramic industry the carbonation products will be developed for further industrial applications.

Results and Discussion

A series of SLs were collected from Italian industries, mainly from ceramic production plants and WtE plants. These were thoroughly characterized, highlighting the peculiar nature of WtE SLs, which are generally mixed with fly ashes from waste combustion, containing high concentrations of easily leachable heavy metals.

To carry out the carbonation of SLs, a semi-batch reaction setup was developed (Figure 1A). This consists of two mass flow controllers that allow precise control of the flow rate and composition of the gas stream entering an autoclave containing a continuously mixed aqueous slurry of the SL. After the autoclave, an on-line gas chromatograph analyses the gas stream, monitoring the process.

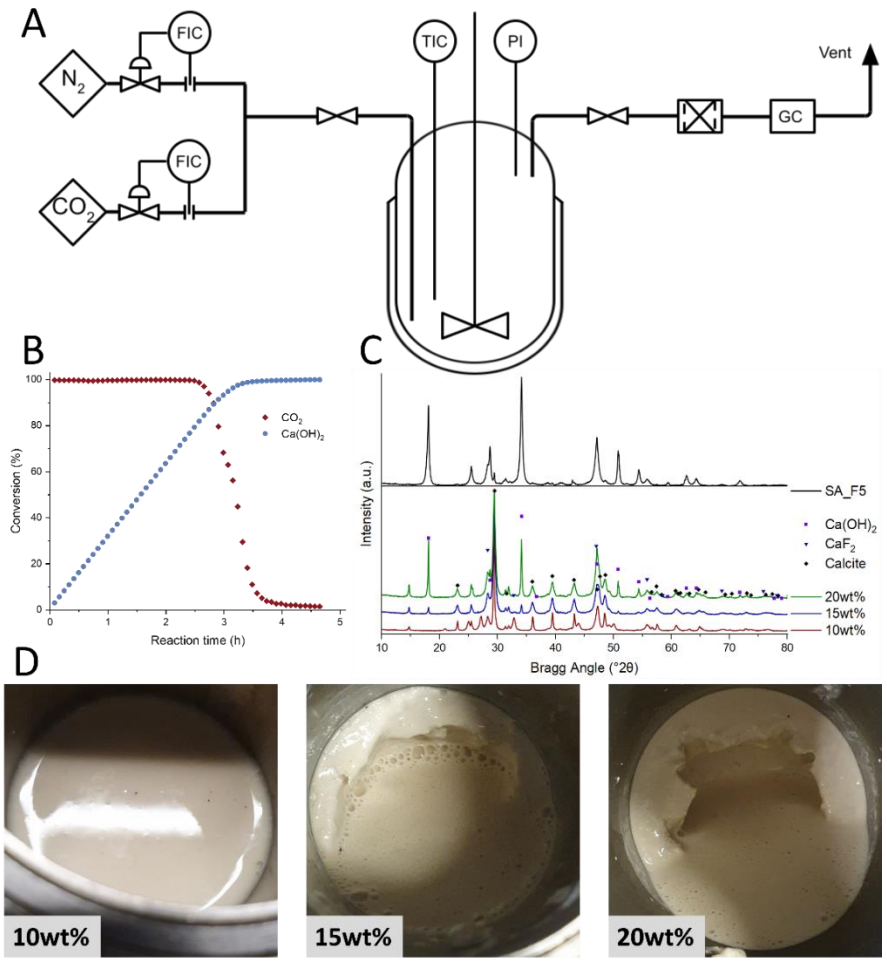


Figure 1. A) Carbonation setup. B) Reaction profile. C) XRPD profiles of a SL sample before and after carbonation. D) Aspect of the slurry after reaction with different amounts of SL.

Various reaction conditions were explored, changing the operating pressure, gas flow and composition as well as the SL slurry concentration. During these studies, valuable insight was gained on the behaviour of this system, and significant improvements were achieved in the development of the process. The collected reaction profiles, with CO_2 conversion and $Ca(OH)_2$ integral conversion presented as a function of carbonation time (an example in Figure 1B), show two valuable results: CO_2 removal from the gas flow is complete as long as $Ca(OH)_2$ conversion is below 90%, demonstrating a high capacity for CO_2 capture even from diluted streams (in this case, 10% CO_2 in N_2); instead, longer reaction times lead to complete conversion of $Ca(OH)_2$ in the SL sample, which is a promising result for the application of the carbonation product in industrial settings. These results could only be achieved after testing the limits of gas-liquid contact provided by the reaction setup and the influence that slurry concentration has on it. This can be observed in Figures 1C and 1D, where slurry concentration is shown to have a drastic effect on mixing and thus the phase composition of the carbonation product.

References

1. A. I. Osman, M. Hefny, M. I. A. A. Maksoud, A. M. Elgarahy, D. W. Rooney, *Environ. Chem. Lett.* **2021**, *19*, 797.
2. R. Millini, M. Bellettato, G. Bellussi, patent WO2021074886A1, assigned to ENI SpA.
3. S. Y. Pan, Y. H. Chen, L. S. Fan, H. Kim, X. Gao, T. C. Ling, P. C. Chiang, S. L. Pei, G. Gu, *Nat. Sustain.* **2020**, *3*, 399.

3D NiMnCo trimetallic electrocatalysts with cauliflower curd-shaped micro-sized nodular morphology for an efficient and sustainable hydrogen evolution reaction in alkaline media and simulated seawater

Sukomol Barua*, Aldona Balčiūnaitė, Jūrate Vaičiūnienė, Loreta Tamašauskaitė-Tamašiūnaitė and Eugenijus Norkus

Center for Physical Sciences and Technology (FTMC), Department of Catalysis, Saulėtekio ave. 3, LT-10257, Vilnius, Lithuania

** sukomol.barua@ftmc.lt*

Significance and Relevance

Hydrogen is a versatile energy carrier, which has the advantages of clean combustion products with zero CO_2 emission, high gravimetric energy density, and large resource reserves, thus, can be one of the potential alternatives to traditional fossil fuel. Electrocatalytic seawater splitting instead of inadequate freshwater is an ideal strategy for the production of green and renewable hydrogen energy. Compared to scarce freshwater, ocean seawater, which covers 97% of the Earth's water reserves, can be considered as an unlimited resource. Thus, seawater splitting could be a more recommended approach than the freshwater electrolysis for sustainable high-purity hydrogen production on an industrial scale.

Preferred presentation: Poster.

Introduction and Motivations

In this work, we report an affordable one-step synthesis of self-supported 3D nickel-manganese-cobalt (NiMnCo) trimetallic coatings, whose electrocatalytic activity and durability were evaluated for the hydrogen evolution reaction (HER) in both alkaline media (1 M KOH) and simulated seawater (1 M KOH + 0.5 M NaCl). These ternary coatings were electrodeposited on a titanium substrate by a straightforward electrochemical deposition using a dynamic hydrogen bubble template technique. Scanning electron microscopy characterization of the optimal NiMnCo/Ti-2 coating revealed a unique cauliflower curd-shaped, micro-nodular architecture with grain particle diameters of 7–14.5 µm.

Materials and Methods

Nickel sulfate hexahydrate ($NiSO_4.6H_2O$, >98%), manganese chloride tetrahydrate ($MnCl_2.4H_2O$, >99%), cobalt nitrate hexahydrate [$Co(NO_3)_3.6H_2O$, >99%] salts were used as a source of metal ions and ammonium sulfate [$(NH_4)_2SO_4$, >99%], boric acid (H_3BO_3, >99.5%), H_2SO_4 (96%) and HCl (35-38%) were the additives used for plating baths. The HER activity of these catalysts was investigated using Linear Sweep Voltammetry in alkaline media and simulated seawater at variuos temperatures. NiMnCo/Ti-1 and NiMnCo/Ti-2 electrocatalysts were synthesized using two electroplating bath solutions containing Ni^{2+}:Mn^{2+}:Co^{3+} molar ratios of 1:5:1 and 1:5:2, respectively.

Results and Discussion

The optimal NiMnCo/Ti-2 electrocatalyst demonstrated excellent HER activity in alkaline media, requiring a low overpotential of 56 mV to reach the benchmark current density of 10 mA cm^{-2}. Impressively, an ultra-low overpotential of 29 mV was needed to achieve the same current density in simulated seawater.

The high-performance NiMnCo/Ti-2 electrocatalyst not only exhibits enhanced HER activity in both electrolytes, but also demonstrates excellent long-term stability, sustaining a constant potential of -0.23 V (vs. RHE) and a constant current density of 10 mA cm^{-2} for 50 hours. In addition, it performed robust performance in a multi-step chronopotentiometry test with current densities ranging from 20 mA cm^{-2} to 100 mA cm^{-2}, indicating sustainable durability and suitability for practical seawater-splitting applications.

Effect of Ni particle size on the efficiency of Ni/HAP catalysts in the decarbonization processes

Nassima Berroug*, Miguel A. Gutiérrez-Ortiz, Juan R. González-Velasco, Zouhair Boukha
Chemical Technologies for Environmental Sustainability Group, Department of Chemical Engineering, Faculty of Science and Technology, University of the Basque Country UPV/EHU, P.O. Box 644, E-48080, Bilbao, Spain
**E-mail: nassima.berroug@ehu.eus*

Significance and Relevance

The impact of the distribution of Ni NP size on the efficiency of a series of Ni(acac)$_2$/HAP-(x) grafted catalysts in the CO_2 methanation reaction has been studied in the present work. These preliminary study points out that this parameter influences the overall activity. In the range of sizes studied (3.9-6.9 nm), it was found that the efficiency is rather improved over the samples with larger particles.

***Preferred presentation*: (Poster)**

Introduction and Motivations

Amid widespread awareness of the importance of green hydrogen (GH2) in technologies designed to reduce global CO_2 levels to acceptable limits, developing novel approaches for its effective application has become essential. However, one of the most debated challenges consists on identifying solutions for the storage and transportation of GH2. In this context, the methanation of anthropogenic CO_2 emerges as a promising approach, allowing the conversion of GH2 into synthetic natural gas (SNG) and, then, taking advantage of the available SNG infrastructures[1,2].

Therefore, the development of active and selective catalysts is of crucial importance for the CO_2 methanation process. The efficient formulations must be capable to reach conversion values close to thermodynamic equilibrium at low temperatures. In parallel, they should be highly selective to methane production. Ni-based catalysts have been extensively investigated owing to their high activity, selectivity and low cost. Nevertheless, they usually suffer from deactivation due to the occurrence of active phases presenting an inadequate distribution. Previous reports associated the suitability of Ni species with a specific distribution of their particle sizes. Some studies have ascibed the efficiency of Ni to its deposition as small particles, whereas other authors linked the activity to larger particles within a specific range of sizes[3,4].

In this contribution, we present our study on the effect of particle size distribution on the efficiency of Ni species grafted onto hydroxyapatite (HAP) support in the CO_2 methanation reaction. For this, the series of catalysts prepared through grafting method have been calcined at 500 °C, by using different temperature ramping rate (TRR).

Materials and Methods

The Ni/HAP catalysts, presenting around 4.5 wt.% Ni, were synthesized by grafting method. First, Ni(acac)$_2$ precursor was dissolved at 60 °C in toluene. Thereafter, the solution temperature was adjusted to 30 °C before adding 3 g of HAP support. The resulting suspension was filtered, washed with pure toluene and, then, dried at 80 °C for 12 h. Finally, the samples were calcined at 500 °C for 4 h, by using different temperature ramping rate (TRR: from 0.5 to 10 °C min^{-1}). The nature of the Ni-HAP interactions have been investigated by using several characterization techniques, including XRF, DRS, TGA, FRX, FTIR, BET, XRD, CO_2-TPD, TPSR, H_2-TPR and TEM microscopy. The experiments corresponding to the CO_2 methanation reaction were performed in a tubular flow reactor (ID = 9 mm) working at atmospheric pressure. The pre-treatment of the catalysts (500 mg, 160-250 µm) consisted of their reduction at 500 °C under a 20% H_2/N_2 for 1 h and cooling to 200 °C in a flow of N_2. The reaction mixture was composed of 16% CO_2, 64% H_2 and 20% N_2, with a total flow of 250 cm^3 min^{-1}, which corresponds to a WHSV of 30,000 cm^3 g^{-1} h^{-1}. For TOF estimation, additional experiments were performed under

differential reactor conditions in the temperature range of 250-350 °C. The analysis system consisted of a gas chromatograph (Agilent 490 Micro GC) equipped with a TCD detector.

Results and Discussion

Table 1 summarizes the properties for the Ni grafted catalysts calcined at 500 ºC with TRR ranging between 0.5-10 °C min^{-1} and reduced at 500 °C (5 °C min^{-1}). The reported data reveal that the particle size generally increases with increasing the temperature ramping rate (3.9 to 6.9 nm). However, no significant change can be observed in the textural properties of the grafted samples.

Table 1. Characterization and activity data for the activated $Ni(acac)_2$/HAP catalysts

Samples	Calcination	TEM	BET			Specific activity	
	Ramping rate, °C min^{-1}	dNi, nm	S_{BET}, $m^2 g^{-1}$	V_p, $cm^3 g^{-1}$	dp, nm	TOF, s^{-1}	Ea, kJ mol^{-1}
HAP		-	51	0.39	27.7	-	-
$Ni(acac)_2$/HAP-(0.5)	0.5	3.9	48	0.34	26.2	0.07	82.3
$Ni(acac)_2$/HAP-(2)	2	5.3	50	0.32	24.4	0.05	84.8
$Ni(acac)_2$/HAP-(5)	5	6.3	50	0.36	25.9	0.11	91.9
$Ni(acac)_2$/HAP-(10)	10	6.9	51	0.33	25.2	0.13	89.1

Fig. 1a displays the evolution of TOF values as a function of the reaction temperature. Unexpectedly, these data point out that the efficiency of Ni species increases with the average particle size increase. Thus, the most efficient catalyst comprises Ni particles exhibiting an average size close to 6.9 nm. Moreover, the activation energy values were estimated from Arrhenius plot (Fig. 1b). According to Table 1, these values are ranging between 82.3 and 91.9 kJ mol^{-1}.

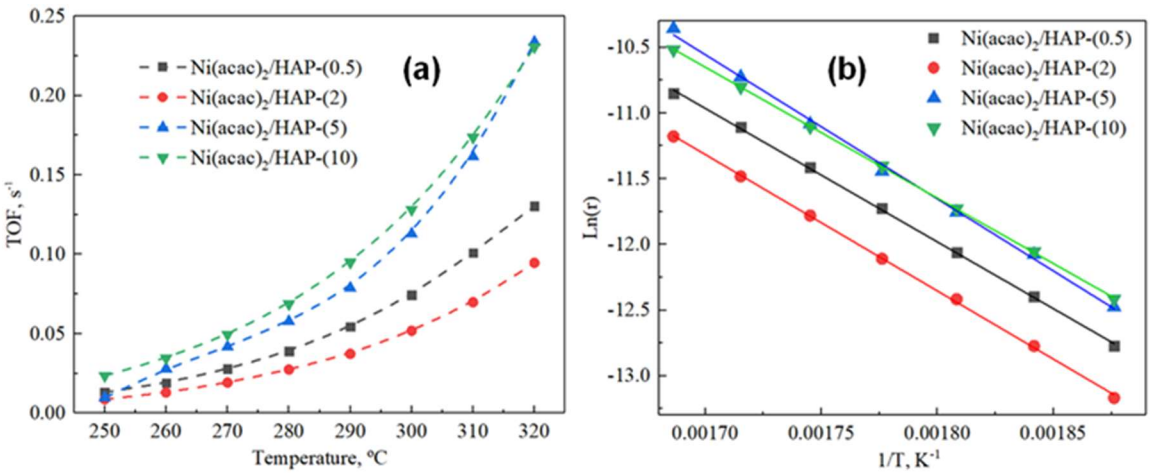


Figure 1. (a) Variation of TOF versus the reaction temperature and (b) Arrhenius plots for the reduced $Ni(acac)_2$/HAP-(x) catalysts

References

1. Z. Boukha, A. Bermejo-López, U. De-La-Torre, J. R. González-Velasco, Appl. Catal. B-Environ. 338 (**2023**) 122989.
2. Z. Boukha, A. Bermejo-López, B. Pereda-Ayo, J. A. González-Marcos, J. R. González-Velasco, Appl. Catal. B-Environ. 314 (**2022**) 121500.
3. N.L. Visser, O. Daoura, P.N. Plessow, L.C.J. Smulders, J.W. de Rijk, J.A. Stewart, B.D. Vandegehuchte, F. Studt, J.E.S. van der Hoeven, P.E. de Jongh, ChemCatChem 14 (**2022**) e202200665.
4. J.K. Kesavan, I. Luisetto, S. Tuti, C. Meneghini, G. Iucci, C. Battocchio, S. Mobilio, S. Casciardi, R. Sisto, J. CO2 Util. 23 (**2018**) 200–211.

Acknowledgements

The authors are indebted to Science and Innovation Ministry (PID2019-105960RB-C21), the Basque Government (IT1509-2022) and I+D+i project CNS2022-135152 funded by MCIN/AEI/10.13039/501100011033/ and the European Union NextGenerationEU/PRTR for the financial support.

Circular Economy-Driven Synthesis of Hydroxyapatites from Ash: A Comprehensive Analysis of Surface and Bulk Properties

Antonella GERVASINI,*[1] Sebastiano CAMPISI,[1] Michele BIGICA,[1] Marta TAVONI,[2] Simone SPRIO,[2] Anna TAMPIERI,[2] Gina POSTOLE[3]

[1] *Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 2013 Milano, Italy*

[2] *Institute of Science, Technology and Sustainability for Ceramics, CNR, Via Granarolo 64, Faenza, Italy*

[3] *Université Claude Bernard Lyon 1, CNRS, IRCELYON, F-69626 Villeurbanne, France*

* *antonella.gervasini@unimi.it*

Significance and Relevance

This study highlights an innovative and sustainable approach to obtaining hydroxyapatites from waste ashes, aligning with circular economy principles by transforming byproducts into valuable, functional materials. Hydroxyapatites are recognized for their applications in biomedicine but also in catalysis, serving as effective sorbents and catalytic materials. The comprehensive analysis of surface and bulk properties provides crucial insights into material performance and potential enhancements. By advancing knowledge in both material sciences and environmental processes, this research supports efforts to valorize waste and promotes the development of greener, resource-efficient materials.

Preferred and 2nd choice for the topic: 1) ***Circular economy****; 2)* ***Fundamental advances in understanding catalysis*** *Preferred presentation*: (***Oral only***)

Introduction and Motivations

The valorization of waste materials has emerged as a critical strategy in sustainable resource management. By rethinking waste as a valuable resource, it is possible to transform it into useful products, thereby reducing environmental impact and conserving natural resources. In this context, calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAP) stands out as a significant biomaterial, naturally found in the hard tissues of mammals, such as bones and teeth, as well as in fish, eggs, and other bio-sources. The ability to derive HAP from waste not only enhances its sustainability but also broadens its applicability in non-conventional application fields, including heterogeneous catalysis and environmental protection. This research explores the potential of waste-derived HAP for use as adsorbent and catalysts in environmental processes where hydroxyapatite has shown success, as water remediation (removing heavy metals from wastewater[1,2]) and air quality protection (CO_2 reduction[3] and NO_x removal[4,5]).

Materials and Methods

The studied samples were obtained from the CNR in Faenza (ISSMC Center) using a three-step extraction process applied to ashes from a waste-to-energy (WTE) plant. The procedure involved: i) dissolution of the ash with obtainment of a leachate enriched in calcium and phosphate ions, ii) crystallization of HAP, and iii) crystal aging/maturation.

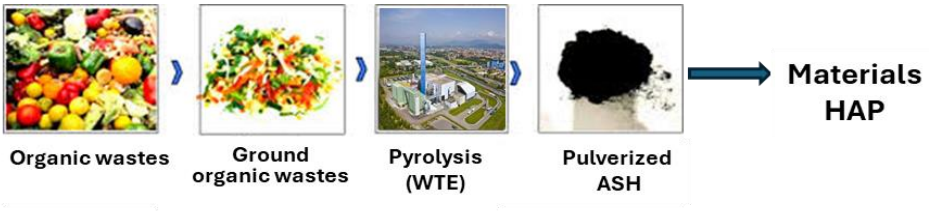


Figure 1. Process chain for obtaining the hydroxyapatite (HAP) samples studied.

The HAP powders were characterized using a suite of techniques to analyze their structure, morphology, and surface properties, including TGA-MS, N_2 adsorption-desorption, TEM-EDX, XPS, FT-IR, Raman spectroscopy, and adsorption microcalorimetry with acidic and basic probes. Comparison was made with a benchmark HAP synthesized in our laboratory.

Results and Discussion

This study presents four different hydroxyapatite samples, labeled HAP-1, HAP-2, HAP-3, and HAP-4, which were obtained using the ash-extraction procedure described above. For their preparation, some process parameters were varied to observe the resulting structural, morphological, and surface characteristics of the samples, as well as to assess the potential scalability of the process.

The elemental composition of the sample was analyzed using EDX spectroscopy. In addition to Ca, P, and O, small traces of other elements (such as Si, Al, Fe, Mg, and Na) were detected. These elements may be present within the structure, potentially substituting for Ca ions. Notably, the typical Ca/P ratio for stoichiometric HAP is 1.67, which was observed when considering the Ca+Mg+Na/P. However, HAP-2 and HAP-3 exhibited higher ratios (Ca+Mg+Na/P≈2.3) suggesting the presence of phases other than hydroxyapatite. XRPD analysis revealed that all the samples exhibited reflections corresponding to the hexagonal structure of stoichiometric hydroxyapatite (JCPDS 00-09-0432) as the sole crystalline phase. HAP-1 and HAP-2 showed higher crystallinity compared to HAP-3 and HAP-4, with the latter being the most amorphous. TEM micrographs of all samples revealed a needle-shaped morphology typical of hydroxyapatite, with highly crystalline domains observed in HAP-1 and HAP-2.

All four samples exhibited the characteristic amphoteric nature of hydroxyapatite's surface, with both acidic and basic sites, similar to the benchmark HAP sample. Adsorption microcalorimetry provided insights into both the number and strength distribution of these sites through the adsorption of NH_3 and SO_2 probes. Figure 2 highlights the results, which show a shift toward basicity in all samples. The strength of the basic sites was notably higher than that of the acidic sites. The most amorphous samples, HAP-3 and HAP-4, exhibited the highest number of both acid and base sites. This was expected in relation to the preparation procedure.

In conclusion, the recrystallization and maturation steps of the ash-extracted procedure were effective in modulating the properties of the resulting hydroxyapatites. The rapid recrystallization and maturation processes produced HAP samples with low crystallinity but a higher number of acid sites and strongly basic surface sites. These characteristics could guide the development of applications in adsorption and/or catalysis. Examples will be presented.

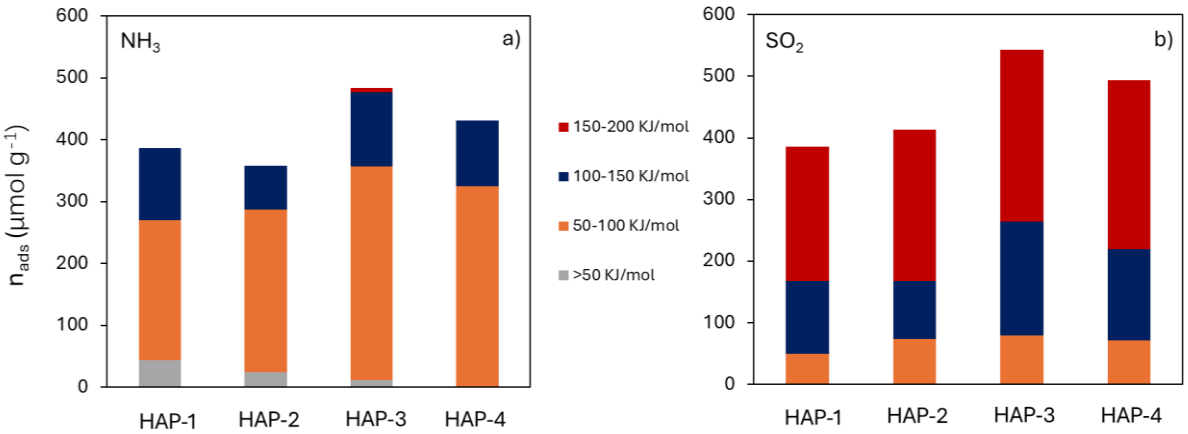


Figure 2. Energy distribution of acid and basic sites in hydroxyapatite (HAP) samples, as determined by NH_3 and SO_2 adsorption microcalorimetry, respectively. The figure compares the relative abundance and strength of acid and basic sites in the different HAP samples studied.

References

1. S. Campisi, C. Castellano, A.Gervasini, New J. Chem. 2018, 42, 4520
2. T. Avola, S. Campisi, L. Polito, S. Arici, L. Ferruti, A. Gervasini, Sci. Rep. 2023, 13, 18913
3. M. Ferri, L. Delafontaine, S. Guo, T. Asset, P. Cristiani, et al., ACS Energy Lett. 2022, 7, 2304
4. S. Campisi, M.G. Galloni, S.G. Marchetti, A. Auroux, G. Postole, A. Gervasini, ChemCatChem 2020, 12, 1.
5. M.G. Galloni, S. Campisi, A. Gervasini, S. Morandi, M. Manzoli, Appl. Catal. A 2023, 655, 119101.

Preparation of Si-rich LTA zeolite for membrane reactors in *e-methanol* synthesis

Lidia Castoldi[1], Luca Lietti[1*], Carlo Visconti[1], Nadia Cerone[2], Francesco Zimbardi[2]
[1]*Politecnico di Milano, Department of Energy, LCCP group, via La Masa 34, 20156 Milano, Italy.*
[2] *ENEA, Energy Technologies and Renewable Sources Department, ss 106, 75026 Rotondella, Italy.*
**luca.lietti@polimi.it*

Significance and Relevance

Membrane technology has attracted considerable interest in both academia and industry due to its benefits, including relatively low energy requirements, reduced operating and capital costs, compact design, and excellent selectivity and separation performance. These advantages have led to membranes increasingly replacing competing technologies across various industrial sectors. Moreover, membranes enable the integration of multiple processes within a single unit, promoting process intensification. For instance, a membrane reactor (MR) can combine chemical reactions and separation within one system. In this respect, zeolite-based catalytic membrane reactors have been successfully applied in overcoming the thermodynamic limitations of methanol synthesis.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling
Preferred presentation: ORAL or SHORT ORAL preferred

Introduction and Motivations

Hydrogenation of CO_2 to methanol with hydrogen obtained from renewable energy (the so-called *e-methanol*), has been proposed as a way of solving two of the main problems that technology is currently facing: the need to reduce CO_2 emissions and the depletion of fossil fuels. One of the drawbacks of this reaction is the low conversion per pass due to the limitations posed by thermodynamic equilibrium. The use of membrane reactors, by removing H_2O and/or MeOH from the reaction environment, have been proposed as a way to improve the methanol per pass yield[1].
In this respect, zeolite membranes have a promising future for applications in membrane reactors (Zeolitic membrane Reactors, ZMRs) due to their selectivity, permeability, and stability concerning higher temperatures and chemically aggressive media. The development of these membranes has focused on the use of inorganic supports with a Si-rich LTA zeolite layer that selectively permeates the water produced by the CO_2 hydrogenation reaction. Indeed, due to the in situ and rapid removal of the produced water from the catalytic layer through the hydrophilic zeolite LTA membrane, it is effective to break the thermodynamic equilibrium limitation, thus significantly increasing the CO_2 conversion and methanol selectivity[2].
In this work the application of LTA zeolitic membranes in e-methanol synthesis has been investigated. Accordingly, a membrane reactor has been designed and ceramic tubes coated with a LTA zeolite layer have been synthesized and characterized in terms of morphology and permeation properties.

Materials and Methods

The synthesis of zeolites begins with the production of seeds through a process without organic structure-directing agents (OSDA), thereby increasing the Si/Al ratio and the resulting stability[2]. These seeds will then be used to create the desired membrane through a second growth step[3].
The zeolite seeds were prepared from a gel with a molar composition of 3.9 Al_2O_3 : 18 SiO_2 : 5 Na_2O : 173 H_2O. For a typical synthesis, $Na_2Al_2O_4$ is dissolved in H_2O and NaOH solution is added to obtain the final Na/Al ratio; the solution was mixed for 60 min. A 40% colloidal silica solution (LUDOX-40) is diluted in H_2O with vigorous stirring at 250 rpm for 60 min. Then, the two solutions were mixed and stirred at 350 rpm for 24 h at ambient temperature; finally, stirring was stopped and the temperature increased up to 67°C and maintained for 7 days. to obtain a uniform hydrogel. After the aging phase, the seeds are washed with H_2O and centrifuged three times, filtered and dried in ambient air[4].
α-alumina tubes are abraded with #4000 sandpaper and washed in boiling water three times to roughen the surface and promote membrane growth, then dried in an oven at 100°C overnight.

The seeds are crushed in a mortar and sieved with a 140-mesh sieve. After wetting the abraded tubes, the seeds are adhered to the surface and then dried for 4 hours at 80°C.
The growth gel is prepared from a solution with a molar composition 0.21 Al_2O_3 : SiO_2 : 0.27 Na_2O : 38 H_2O, using the same procedure of seeds synthesis with 6 hours of stirring. The seeded supports, 10 - 15 cm length, were subsequently immersed into a Teflon-lined stainless-steel autoclave filled with the synthesis gel for the hydrothermal reaction. The autoclave was placed horizontally in the oven at 120°C at different times. The obtained membranes were washed in H_2O and dried overnight at 80°C.

Results and Discussion

As-synthetized Si-rich LTA shows a typical type IV N_2 adsorption-desorption isotherm (Fig. 1A). The average mesopore size results of 39 nm and BET surface area 30 m^2/g_{cat}.
The characterization of the seeds was performed through XRD analysis (Fig.1B), which shows patterns consistent with the desired LTA zeolite, and no sodalite (SOD) phase is observed[4]. The Fig. 1C shows characteristic FT-IR[5] bands of as-synthesized LTA zeolite: i) the 3378 cm^{-1} broad band is assigned to the stretching of H bridges attributed to the interaction between physically adsorbed water and surface oxygen; ii) vibrations around 1641 cm^{-1} are attributed to the bending of the OH group in adsorbed water; iii) vibrations reflected at 1000 cm^{-1} are assigned to the asymmetric stretching vibrations characteristic of Si–O (Si) and Si-O (Al) bridge bonds in TO_4 tetrahedra belonging to aluminosilicates; iv) the 665 cm^{-1} band is assigned to the symmetrical stretching vibrations of the Si-O-Al bond bridges.
SEM image of LTA zeolite deposited over the alumina tubes for different maturation times (Fig. 2) shows the crystallization habits of the as-synthesized zeolite. In general, the sample consists of particles aggregates and isolated ones with well-developed faces and defined edges showing cubic and, in some cases, cubic-octahedral shapes. The crystal shape observed is consistent with the assigned space group *Fm3c* for LTA zeolite. Increasing the maturation time increases the homogeneity of the zeolite layer. Experiments are on-going to characterize the permeability of the prepared membranes towards methanol/water mixtures.

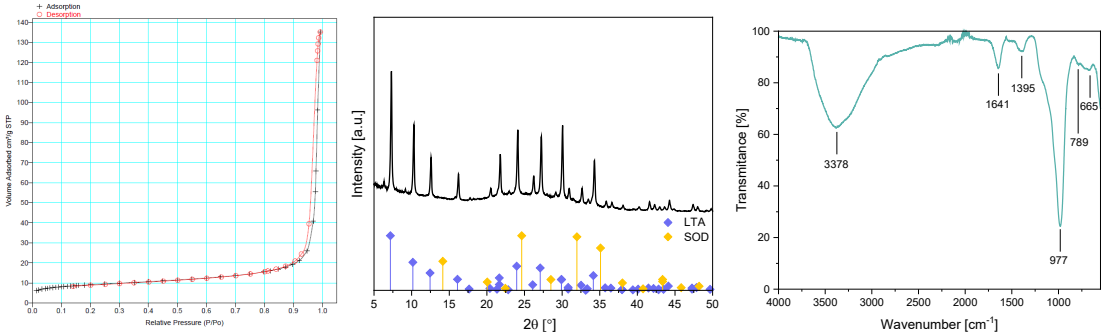


Figure 1 - A) N_2 adsorption-desorption isotherm; B) XRD analysis; C) FT-IR analysis

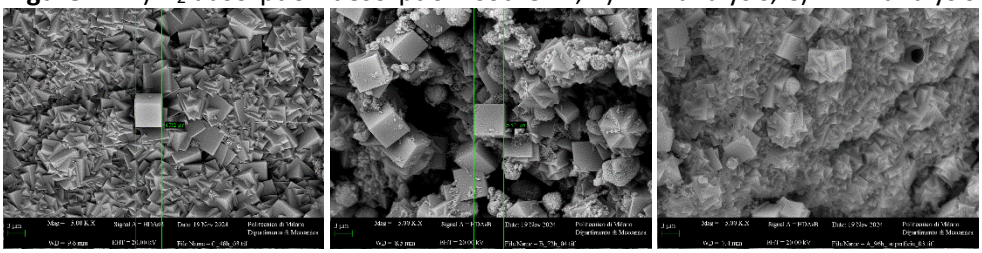


Figure 2 - SEM images of alumina coated tubes at different maturation times: 48h, 72h, 96h (5.00kX)

References

1. M. Seshimo, B. Liu, H. Ryeon Lee, K. Yogo, Y. Yamaguchi, N. Shigaki, Y. Mogi, H. Kita, S. Nakao, *Membrane* **2021**, *11*, 505
2. W. Yue, Y. Li, W. Wei, J. Jiang, J. Caro, A. Huang *Angewandte Chemie - International Edition* **2021**, *60*, 18289
3. B. Liu, H. Kitaa, K. Yogo, *Sep Purif Technol* **2020,** *239*, 116533
4. A. Jacas-Rodríguez, P. Rodríguez-Pascual, D. Franco-Manzano, L. Contreras, C. Polop, M.A. Rodriguez, *Sci Eng Compos Mater* **2020**, *27*,236
5. W. Mozgawa, M. Król, K. Barczyk, K. *CHEMIK* **2011**, *65*, 667

Synthesis of sustainable polyol by simultaneous utilization of CO_2 and waste PET

Jiyoung Chae, Yein Kim, Joon Hyun Baik*
Department of Chemical and Biological Engineering, Sookmyung Women's University, 04310, Seoul, Republic of Korea
** joonhyun@sookmyung.ac.kr*

Significance and Relevance

This study proposes a novel approach for two key environmental issues: waste PET upcycling and CO_2 utilization. By glycolyzing waste PET bottles, high-purity bis(2-hydroxyethyl) terephthalate (BHET) was synthesized and used as an initiator in the copolymerization of CO_2 and propylene oxide (PO) to produce sustainable polyols. The PET-CO_2 polyols were successfully produced using a double metal cyanide (DMC) catalyst under various reaction condition including CO_2 pressures and PO/BHET feed ratios. These PET-CO_2 polyols were utilized to synthesize flexible polyurethane foams with comparable properties of commercial polyurethane.

Preferred and 2nd choice for the topic

1. CO_2 utilization and recycling
2. Green chemistry and biomass transformation, Renewable resources conversion

Preferred presentation: Poster

Introduction and Motivations

Effective carbon capture and recycling methods are essential, as the climate changes induced by CO_2 emissions and plastic waste are increasingly recognized as significant global challenges. In this study, waste PET was converted into BHET, which initiates the copolymerization of CO_2 and PO to yield PET-CO_2 polyol. This innovative approach not only recycles PET but also utilizes CO_2 to produce valuable polyols, offering a sustainable solution that mitigates pollutants and supports various industrial applications.

Results and Discussion

Production of BHET via glycolysis of waste PET

The glycolysis of waste PET (5 g) was carried out using ethylene glycol (50 g) and MgO catalyst (200 mg) at 190°C for 3 hours, resulting in a PET conversion of 92.6% and a BHET yield of 64.7%. The structural properties of the synthesized BHET were characterized by FTIR and ^{1}H NMR spectroscopy (**Figure 1**) and compared to those of commercial BHET (Sigma-Aldrich). In the FTIR spectra (**Figure 1a**), both synthesized and commercial BHET showed characteristic bands. A broad peak at 3436 cm^{-1} corresponds to O-H stretching, while peaks at 2964 cm^{-1} and 2880 cm^{-1} indicate asymmetric and symmetric C-H stretching of methylene groups[1]. The strong peak at 1713 cm^{-1} reflects C=O stretching, with additional peaks at 1503 cm^{-1}, 1686 cm^{-1}, and 724 cm^{-1} corresponding to aromatic C-H and benzene ring vibrations. The ^{1}H NMR spectra (**Figure 1b**) showed 8.12 ppm for aromatic protons, and 4.95 ppm for terminal -OH protons. 4.32 and 3.72 ppm indicate protons in methylene groups. Additionally, a peak at 4.68 ppm reveals BHET oligomers[2], which were present in commercial BHET but absent in the synthesized BHET, suggesting higher purity in the latter.

These results demonstrate the effective synthesis of high-purity BHET from waste PET via glycolysis. The absence of oligomeric impurities in the synthesized product highlights the potential of this method for producing high-quality monomers, contributing to the development of sustainable recycling strategies.

Synthesis of PET-CO_2 polyol

The Zn-Co double metal cyanide (DMC) catalyst with poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (P123) as a complexing agent was employed since this catalyst showed effective for CO_2 insertion in polypropylene carbonate (PPC) synthesis in our research[3]. Copolymerization was conducted under various CO_2 pressures (5, 10, 15, and 20 bar) and PO/BHET molar ratios (33.33, 50, 66.67, and 100), allowing detailed analysis of CO_2 pressure and reactant ratios on PET-CO_2 polyol properties.

Figure 2 presents FTIR and ^{1}H NMR spectra of the polyols synthesized under these conditions. **Figure 2a** shows spectra of polyols prepared with different CO_2 contents, and **Figure 2b** shows the effects of varying PO/BHET feed ratios on the structures of polyols. In the FT-IR spectra (**Figure 2a**), key peaks at 1742 cm^{-1} and 1264 cm^{-1},

corresponding to C=O and C-O stretching of carbonate units, increased with higher CO_2 content, indicating more carbonate incorporation. The ^1H NMR spectra also showed increasing intensities of carbonate proton peaks (4.8–4.9 ppm for C-H, 1.2–1.3 ppm for CH_3, and 3.8–3.9 ppm for CH_2), confirming greater CO_2 incorporation. **Figure 2b** shows polyols synthesized at different PO/BHET ratios. As the PO/BHET ratio increased, the carbonate C=O stretching peak at 1742 cm^{-1} intensified, while the BHET C=O peak decreased. Additionally, the O=C-O group peak at 754 cm^{-1} increased, while the aromatic C-H peak of BHET at 730 cm^{-1} diminished. The ^1H NMR spectra mirrored these trends, with BHET-related peaks (aromatic proton at 8.1 ppm and methylene protons at 4.4–4.6 ppm) increasing with higher BHET content, while peaks for carbonate units (C-H at 4.8–5.0 ppm and CH_3 at 1.25 ppm) decreased as BHET content increased. These observations suggest that a higher BHET feed reduces the incorporation of CO_2 into the polyol structure, thereby decreasing the proportion of carbonate units. This can be attributed to the reduced availability of CO_2 for copolymerization as the initiator BHET content increases, limiting its integration into the polymer chain.

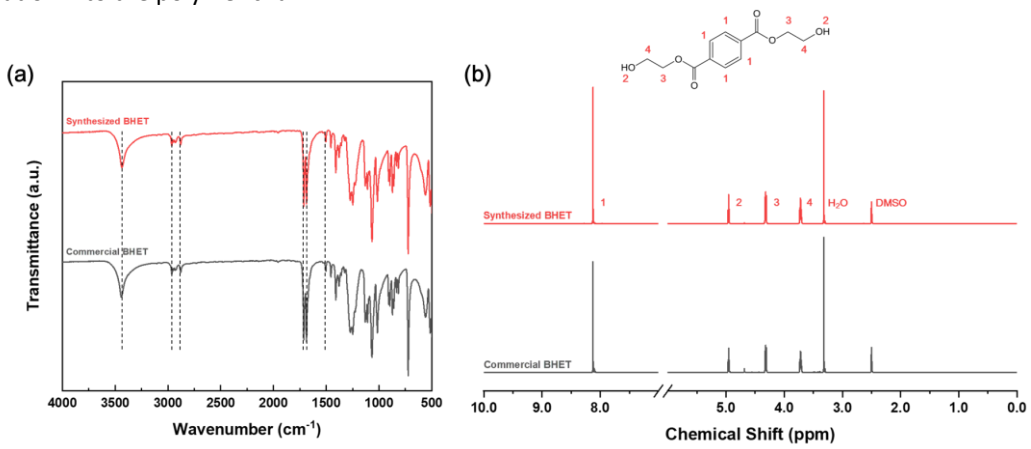


Figure 1 Structural properties of synthesized and commercial BHET monomer. (a) FTIR and (b) ^1H NMR spectra.

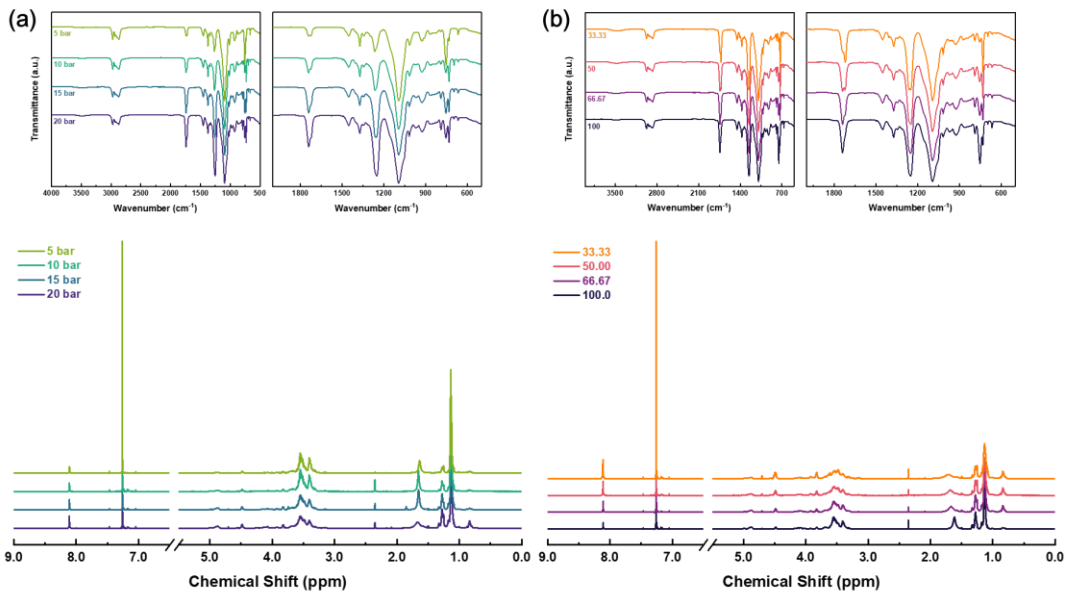


Figure 2 Structural properties of PET-CO_2 polyols. FTIR and ^1H NMR spectra of (a) various CO_2 content and (b) PO/BHET molar ratio.

References

1. C. Zhang, *Ind. Eng. Chem. Res.* **2024**, *25*, 10903-10913.
2. S. Mohammadi, *ACS Appl. Polym. Mater.* **2023**, *8*, 6574-6584.
3. H. Kim, *ACS Omega* **2023**, *42*, 39279-39287.

Understanding Methanation Inhibition Using Cs-promoted Defective Carbon Supports for Ru Catalysts in Ammonia Production

Cheng-Hsi Yeh[1], Hsin-Yu Chen[1,2], Shih-Yuan Chen[3], Hsin-Yi Tiffany Chen*[,1,2,4]
[1] *National Tsing Hua University, Department of Engineering and System Science, Hsinchu 300044, Taiwan.*
[2] *National Tsing Hua University, Department of Materials Science and Engineering, Hsinchu 300044, Taiwan.*
[3] *National Institute of Advanced Industrial Science and Technology (AIST), Energy Catalyst Technology Group, Energy Process Research Institute (EPRI), 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan.*
[4] *National Tsing Hua University, College of Semiconductor Research, Hsinchu 300044, Taiwan.*
** hsinyi.tiffany.chen@gapp.nthu.edu.tw*

Significance and Relevance

Our study investigates the role of Cs promoters and vacancy of carbon support in ammonia production, focusing on hydrogen spillover leading to methanation issues. Using density functional theory (DFT), we explored the role of the Ru-carbon interface, carbon vacancies, and Cs promoters. Our findings reveal that the vacancies of carbon supports and CsOH promoters are crucial in reducing methanation. This insight highlights the importance of support material properties and promoter effects in enhancing catalyst stability and activity, offering strategies for catalysts design in hydrogen-related reactions.

Preferred and 2nd choice for the topic: Fundamental advances in understanding catalysis, Multiscale modeling and advanced simulation aspects
Preferred presentation: Poster

Introduction and Motivations

Ru-based catalysts, produced using the Kellogg Advanced Ammonia Process (KAAP) and supported on graphite, are widely used in industrial ammonia synthesis. However, methanation through hydrogen spillover on these carbon-supported Ru catalysts poses a significant problem, reducing both catalyst stability and activity. Experimental results have shown that adding a Cs promoter and altering the graphitization degree of carbon supports can reduce methanation.[1] However, the mechanism behind this reduction remains unclear. To address this, we used density functional theory (DFT) to investigate the role of the Ru-carbon interface, carbon vacancies, and promoters in carbon support methanation. Our results indicate that the synergistic effect of the graphitization degree of carbon supports and the promoter is crucial for reducing methanation.

Materials and Methods

Spin-polarized DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP). The Ru and Cs promoted Ru cluster were bound to a 7 × 7 supercell of the vacancy graphene (VG) with dimensions a = 17.27 Å, b = 17.27 Å, and c = 20 Å. Adsorption energy per hydrogen atom was using the equation $E_{ads} = (E_{nH/cat} - E_{cat} - n \times 0.5 \times E_{H2})/n$ to calculate, where $E_{nH/cat}$ represents the total energy of hydrogen adsorption on the VG supported Ru or Cs promoted Ru catalyst models, E_{cat} denotes the total energy of the bare catalyst models, n symbolizes the number of H atom adsorbed, and E_{H2} is the total energy of the H_2 molecules.

Results and Discussion

In our previous study, we used a single Ru atom on graphene to understand the role of Cs promoters. CsOH acts as a spillover site for hydrogen, lowering the activation barrier for hydrogen spillover.[1] To further investigate the hydrogen spillover pathway and the effect of vacancies on the carbon support, we built a model with Ru_8 cluster on graphene with two vacancies (Ru_8/VG), as shown in Figure 1(a). The Ru_8 cluster is the smallest size to model the B_5 active site. Of the two vacancies on graphene, one anchors the Ru_8 cluster, and the other facilitates hydrogen spillover. In the previous study, the Cs

promoter was found between the Ru and carbon support interface.[2] Therefore, we placed CsOH near the Ru_8 model (CsOH–Ru_8/VG, Figure 1(b)) to discuss the mechanism with and without CsOH.

Our results show that as more hydrogen atoms are adsorbed on Ru_8/VG, the $E_{ads/H}$ values become more positive, indicating weaker hydrogen adsorption strength with increased coverage. When a hydrogen atom spills over to the top site of graphene, the $E_{ads/H}$ values of the spillover structure are always more positive than those of non-spillover structures. Conversely, when hydrogen atoms spill over to a vacancy on graphene, the $E_{ads/H}$ values of the spillover structure are always more negative than those of non-spillover structures (Figure 1(c)). These findings indicate that high graphitization degree (graphene without defects) in carbon supports prevent hydrogen spillover to the support, leading to methanation. In contrast, carbon materials with vacancies facilitate hydrogen spillover, resulting in methanation on carbon supports.

For the CsOH–Ru_8/VG system, when hydrogen spills over to graphene, the $E_{ads/H}$ values indicate that the preferred site for spillover is the vacancy, similar to the result for Ru8/VG. However, in the absence of a vacancy, hydrogen will spill over to the OH group of CsOH at high hydrogen coverage. This result demonstrates that the Cs promoter and the vacancy of carbon materials play crucial roles in reducing hydrogen poisoning and methanation. A higher graphitization degree of carbon materials reduces carbon support methanation, while CsOH provides an additional spillover site to mitigate hydrogen poisoning.

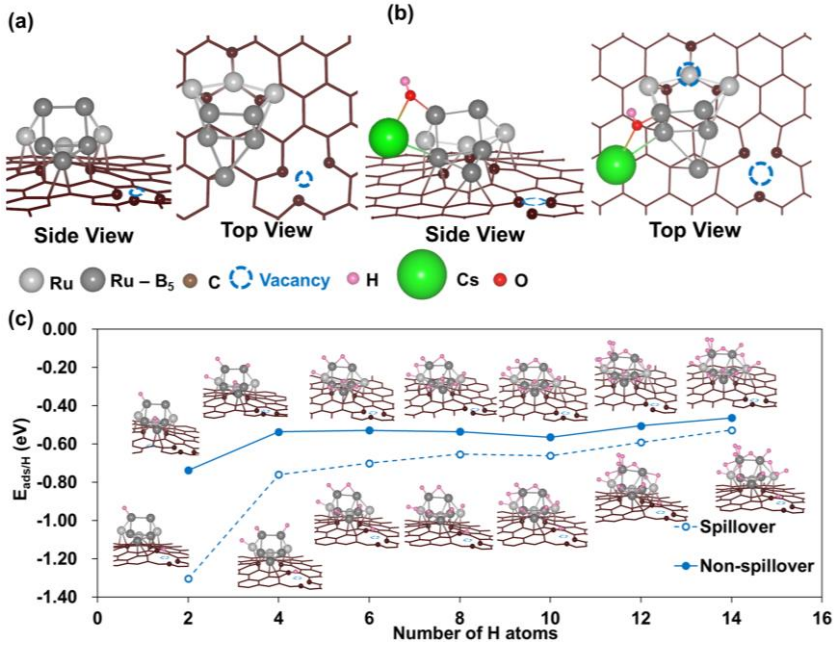


Figure 1 (a) Optimized structure of Ru_8/VG. (b) Optimized structure of CsOH-Ru_8/VG. (c) Adsorption energy per hydrogen ($E_{ads/H}$) of non-spillover and spillover with different numbers of H atoms on Ru_8/VG. Atom color: grey: Ru atoms, dark grey: Ru atoms of B_5 site, brown: carbon atoms, blue dash line: vacancy, pink: hydrogen atoms, green: Cs atom, and red: O atom.

References

1. S.-Y. Chen, L.-Y. Wang, K.-C. Chen, C.-H. Yeh, W.-C. Hsiao, H.-Y. Chen, M. Nishi, M. Keller, C.-L. Chang, C.-N. Liao, T. Mochizuki, H.-Y. T. Chen, H.-H. Chou and C.-M. Yang, *Applied Catalysis B: Environment and Energy*, 2024, **346**, 123725.
2. Z. Kowalczyk, M. Krukowski, W. Raróg-Pilecka, D. Szmigiel and J. Zielinski, *Applied Catalysis A: General*, 2003, **248**, 67–73.

Acknowledgements

Acknowledge National Science and Technology Council, NSTC (111-2221-E-007-087-MY3, 111-2112-M-007-028-MY3) and National Tsing Hua University (113QI021E1, 113Q2773E1) in Taiwan for their financial support. The computational resources were supported by TAIWANIA at the National Center for High-Performance Computing of National Applied Research Laboratories in Taiwan.

Photocatalytic CO_2 reduction over $TiO_2NT/g\text{-}C_3N_4$ based heterostructures

Imen CHERIF, Georgia PAPANIKOLAOU, Paola LANZAFAME, Siglinda PERATHONER, Gabriele CENTI, Rosalba PASSALACQUA*

University of Messina, Department of Chemical, Biological, Pharmaceutical and Environmental Sciences (ChiBioFarAm) & INSTM CASPE (Lab. of Catalysis for Sustainable Production & Energy), Viale F. Stagno d'Alcontres 31, 98166 Messina, Italy

** rpassalacqua@unime.it*

Significance and Relevance

Photocatalytic reduction of carbon dioxide (CO_2) to produce energy fuels is presented by using a novel $TiO_2NT/g\text{-}C_3N_4$ heterostructure. The heterostructure formation imparts unique characteristics enhancing the CO_2 adsorption and activation efficacy with respect to the bare components. Moreover, composite fabrication is by far the most efficient method to improve charge carrier separation efficiency.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling / Photocatalysis and photoelectrocatalytic approaches, solar energy utilization
Preferred presentation: Short Oral / Poster

Introduction and Motivations

An attractive approach to addressing two of the main environmental concerns, namely fossil fuel dependency and environmental pollution due to greenhouse gases, is photocatalytic CO_2 reduction, on TiO_2 tubular nanostructures coated with $g\text{-}C_3N_4$. The polymeric carbon nitride ($g\text{-}C_3N_4$) shows great potential for photocatalytic CO_2 reduction because of its suitable conduction band position, which satisfies the thermodynamic condition of most CO_2 reduction reactions.[3] In recent years, investigations on metal-based semiconductors have received broad attention, especially using TiO_2, ZnO, CdS, Cu_2O. Here a hybrid structure has been explored performing the process under mild reaction conditions with an increased conversion yield and controlled selectivity. The nanostructured TiO_2 semiconducting material was developed to improve the visible-light absorption, sustainability and stability of the system and to enhance the photocatalytic performance by suppression of the photogenerated carriers.

Materials and Methods

The tubular-shaped TiO_2 array has been fabricated by anodic oxidation (AO) of a metallic titanium substrate in ethylene glycol electrolyte containing 0.3 wt. % NH_4F, and 2% vol. H_2O. Then, the self-ordered TNTs surface was decorated with graphitic carbon nitride ($g\text{-}C_3N_4$) prepared by a simple thermal heating and condensation method. Typically, the polymeric carbon nitride was prepared by placing 2 g of melamine in a porcelain crucible with the anodized TNTs disc as a cover, then the precursor was heated to 550 °C for 3 h in a muffle furnace at atmospheric pressure in air. [1]

The prepared material has been characterized by chemical–physical, morphological, and structural investigations, then the functional properties of the composite have been studied by electrochemically by chronoamperometry experiments under dark and illuminated conditions and linear sweep voltammetry. Finally, the materials have been tested in the electrocatalytic CO_2 reduction reaction.

Results and Discussion

Aimed at reducing environmental impact, we have developed a new photo-assisted route for electrochemical conversion of CO_2 by using a new composite heterostructure identified as $TiO_2NT/g\text{-}C_3N_4$.

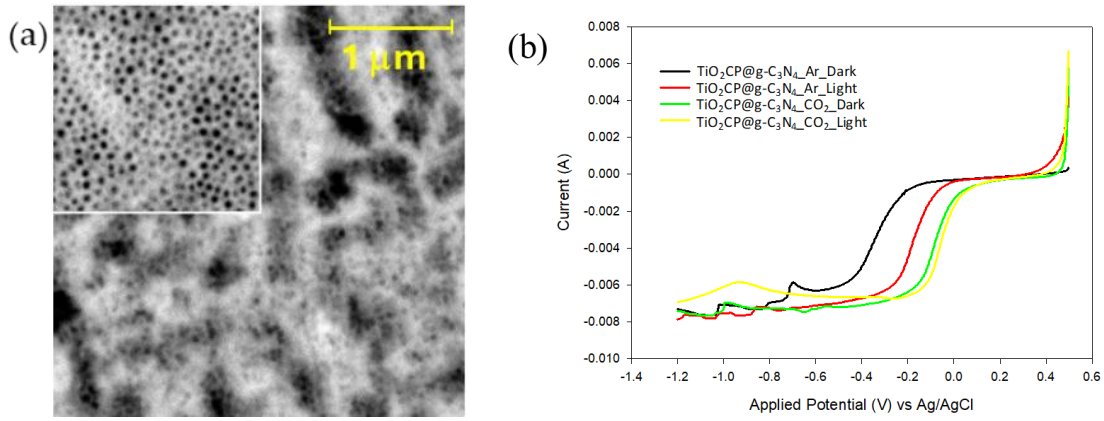


Figure 1a, SEM images of the composite and of bare TiO_2NT array, left side insert. **Figure 1b** reports the LSW curves acquired in 0.5 M Na_2SO_4 under Argon and CO_2 as an example of the electrochemical characterization of the composite.

Figure 1a shows the SEM image of the composite and that of the bare TiO_2NT array in the insert on the left, highlighting a highly ordered and uniform pore structure of the nanotubes which is ideal and beneficial for the adsorption of the polymeric g-C_3N_4. **Figure 1b** reports the linear sweep voltammetry (LSW) curves acquired under Argon and CO_2 evidencing the positive shift (~120mV) of the potential under illumination in the case of CO_2.

XPS measurements have been acquired for investigating the electronic structure of the g-C_3N_4/TNT composite material and to confirm the prepared samples' chemical composition and valence state. For the composite, a shift to a higher binding energy and an increase in the electronic signal have been observed, indicating an interaction between the polymeric moiety and the TiO_2 nanotubes, and an increased electron density on Ti compatible with a charge transfer from the electron-rich g-C_3N_4 surface to the unoccupied orbital of Ti^{4+}.[2] This observation confirms the interaction between the two components and, ultimately, the effective preparation of the heterojunction.

The prepared material has been tested in photo-assisted electrocatalytic reduction of CO_2, serving as cathodic electrode, in a full electrochemical cell employing different solutions (0.1 M $KHCO_3$ and 0.5 M k_2SO_4) as circulating electrolyte and a Pt plate as anode. The reduction products were monitored under potentiostatic electrolysis to confirm the occurrence of CO_2 reduction.

References

1. R. Passalacqua, S. Abate, F. De Luca, S. Perathoner, G. Centi, *Coatings* **2023**, *13*(2), 358.
2. C. Liu. F. Wang. J. Zhang. K. Wang. Y. Qiu. Q. Liang. Z. Chen, *Nano-Micro Lett.* **2018**, 10:37.
3. Y. Fang and X. Wang, *Chem. Commun.* **2018**, 54, 5674.

Acknowledgements

This work was realised in the frame of the activities of PRIN project BOMBCAT (code P202253ANE) funded by the Italian Ministry for Universities under the National Recovery and Resilience Plan (NRRP).

Influence of preparation method of CuAl mixed oxide issued from LDH for LDH for catalytic total oxidation of VOC -CO

Eric GENTY*, Pierre Edouard DANJOU, Christophe POUPIN, Stéphane SIFFERT, Renaud COUSIN
Université du Littoral Côte d'Opale, Unité de Chimie environnementale et Interactions sur le Vivant (UCEIV), 145 avenue Maurice Schumann, 59140 Dunkerque, France.
eric.genty@univ-littoral.fr

Significance and Relevance

This work proves that it is possible to produce highly efficient catalysts issued from LDH precursors with low synthesis duration. Catalytic performance challenges the expensive noble metal-based systems for this this type of application. Moreover, the complexification of reaction mixture enhances the total oxidation of toluene indicating potential applications of this type of materials for the depollution of fumes issued from biomass combustion.

Topics: Air cleaning and combustion or Automotive and stationary emission control and Presentation preferred: *Oral only*

Introduction and Motivations

Emissions of VOCs into the environment is now strictly regulated due to harmful to public health and atmospheric environment and are often accompanied with CO in industrial and combustion fumes. In the aim to obtain a reaction economically competitive, it is necessary to explore higher active catalysts performing. Transition metal oxides, especially Co, Cu and Mn oxides, offer a low-cost alternative to metal noble based catalysts which are presently the most active catalysts in the complete oxidation of VOCs at low temperatures. An interesting way to obtain mixed oxides catalysts is through the use of layered double hydroxides (LDH) as precursors. The coprecipitation is the method widely applied for the LDH synthesis but recently, microwaves (MW) and ultrasound (US) have been applied as an alternative to the conventional treatments [1-3]. Several advantages such as shorter treatment times to achieve enhanced crystallinity degrees, higher specific surface areas, and increase the metallic dispersion are reported. In this study, CuAl LDH as precursors are characterized and investigated for total oxidation of CO and Toluene mixture.

Materials and Methods

LDH precursors Cu_6Al_2 were prepared by three methods (conventional synthesis (CT), MW treatment and US treatment) and calcined at 500°C before physicochemical characterizations. Catalytic tests were made using a gas mixture containing of 1000 ppm C_7H_8 and/or 1000ppm CO and air flow.

Results and Discussion

A beneficial effect of a MW and US method was observed on the preparation of mixed oxides. The characterization of these solids revealed several textural and physicochemical differences (specific surface areas, crystallites size, reducibility, …). The use of MW or US synthesis procedure was induced a variation of Cu/Al atomic ratio on the surface and O_{ads}/O_{bulk} observed by XPS analysis. Catalytic performances for toluene oxidation in presence or absence of CO according the T_{50} values shows an increase of activity for the solid prepared by US and MW. Relations between physicochemical properties and catalytic activity have been established (Figure 1), indicating a Mars Van Krevelen mechanism for toluene total oxidation in presence of CO in the reactional mixture.

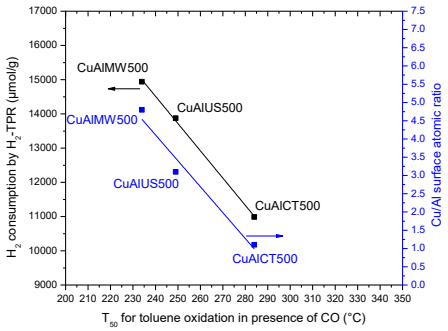


Figure 1 Relation between catalytic activity and physicochemical properties

References

1. Genty E, Brunet J, Poupin C, Casale S, Capelle S, Massiani P, *et al*. Catalysts. 2015;5(2):851–67.
2. M. Climent, A. Corma, S. Iborra, K. Epping, A. Velty, 2004 J Catal 225 316.
3. P. Benito, F.M. Labajos, V. Rives, 2009 Pure Appl. Chem 81 1459.

Acknowledgements

The authors gratefully acknowledge the financial support from the CPER-ECRIN program, the Hauts-de-France region and the European Community (Interreg Vi France-Wallonie-Vlaanderen project, "CleanAirBouw").

Utilization of visible light in the Reverse Water Gas Shift reaction over $Cu/Ce_x(Ti_{1-x})O_2$ catalyst

Miha Okorn[1,2], Kristijan Lorber[1] and Petar Djinović[*1,2]
[1]*National Institute of Chemistry, Hajdrihova 19, Ljubljana, Slovenia.*
[2] *University of Nova Gorica, Vipavska 13, Nova Gorica, Slovenia.*
** petar.djinovic.si*

Significance and Relevance

The $Cu/Ce(Ti)O_2$ nanorod catalysts demonstrate significant potential for the light-assisted conversion of CO_2 to CO. During the light-assisted reaction, the activation energy (E_a) decreased substantially, leading to a significant increase in the CO formation rate and apparent change in the reaction mechanism compared to the thermally driven reaction. Furthermore, this contribution will present our latest research on catalyst structural characterization and in-situ spectroscopic analysis to better understand the influence of visible light on the reaction mechanism of the Reverse Water-Gas Shift (RWGS) reaction.

Preferred and 2nd choice for the topic: Photocatalysis and photoelectrocatalytic approaches, solar energy utilization and CO_2 utilization and recycling
Preferred presentation: Oral preferred or short oral

Introduction and Motivations

The Reverse Water Gas Shift (RWGS) reaction presents an intriguing pathway for reducing CO_2 to valuable CO using renewable H_2. [1] Light-assisted catalysis, which synergistically combines thermal and light energy, offers a promising approach to accelerate the RWGS reaction. Ceria-based catalysts have gained a lot of interest in the CO_2 conversation processes, particularly in the form of nanorods which demonstrate higher catalytic activity among the different CeO_2 morphologies. [2] Modifying the CeO_2 nanorods with specific oxides like TiO_2 (a known photocatalyst)[3] and copper (with its unique plasmonic properties)[4] could potentially benefit the photo-thermal RWGS reaction by optimizing the absorption and utilization of visible light, improving surface properties of the support, forming additional active sites for H_2 and CO_2 activation, consequently leading to final CO formation. This approach can significantly reduce the energy input required for the traditional RWGS reaction while increasing CO_2 conversion and subsequent CO formation.

Materials and Methods

We synthesized Ti-doped (2 mol.%) CeO_2 nanorods as support and then deposited 1, 3, 8 and 30 wt.% of copper by wet impregnation. Using only visible light, we were able to compare thermal and light-assisted performance of the catalyst. The experiments were conducted in a fixed-bed reactor, where the analyzed temperature range was 200-320 °C at ambient pressure and the total flow rate of inlet gas mixture (CO_2/H_2 =1/1) was kept constant at 30 ccm during both thermal and light-assisted processes. Detailed characterization included SEM, XRD as well as *in-situ* UV-Vis and transient DRIFT spectroscopy for analysis of the catalysts optical absorption, oxygen defects and surface species in dark and under light-assisted conditions.

Results and Discussion

XRD analysis revealed that initial titanium doping expanded the CeO_2 crystal lattice due to the inclusion of Ti^{4+} ion into the CeO_2 crystal lattice, while Cu nanoparticles were dispersed on the surface of the support. Catalytic experiments demonstrated that all titanium-doped catalysts (xCu-CeTi) exhibited higher CO formation rates (R_{CO}) than undoped CeO_2 catalysts during light-assisted reactions (Figure 1A), suggesting a synergetic effect of titanium addition to CeO_2 nanorods and visible light. The catalyst containing 3 wt.% of Cu displayed the highest catalytic activity in both dark and light-assisted

conditions. As shown in Figure 1B, temperature dependent experiments indicated an increase in the activity of the 3Cu-CeTi catalyst with temperature, without any sings of deactivation under either reaction conditions. The catalyst shows no catalytic activity below 213 °C in dark, while significant activity (0.24 mmol CO/g_{cat}*min, catalyst temperature of 116 °C) was observed under light-assisted reaction without additional electric heating. Additionally, Arrhenius plots for the 3Cu-CeTi catalyst (Figure 1C) show a substantial decrease in apparent activation energy upon illumination, from 92 to 26 kJ/mol, indicating an alteration in the energetics of the rate-determining step of the RWGS reaction. Wavelength dependent experiments revealed that simultaneous excitation of copper and ceria support result in apparent quantum yields that are about two times higher compared to excitation of copper phase. Furthermore, transient operando DRIFTS experiments showed that illumination accelerates carbonate hydrogenation (to formate), and hydrogen-assisted formate dissociation to CO and H_2O, revealing the underlying origins of accelerated CO rate.

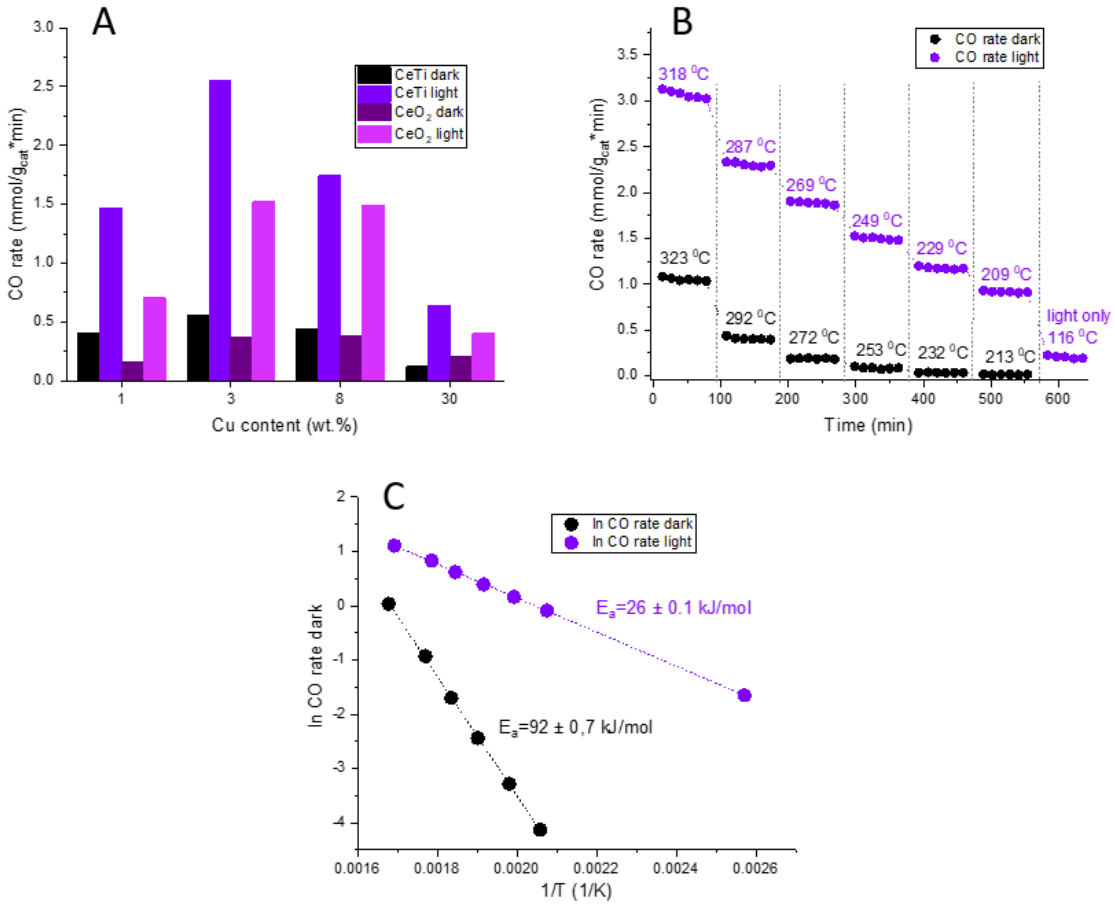


Figure 1: A) CO rate comparison under thermocatalytic and light-assisted conditions of different Cu loadings deposited on CeTi and CeO_2 supports using H_2/CO_2 feed ratio of 1/1 at 300 °C. B) Temperature dependence of the CO rate over the 3Cu-CeTi catalyst under dark and light-assisted conditions. C) Apparent activation energies under dark and light-assisted conditions.

References

1. F. Fresno et all, Topics in current chemistry, 2023, 381(21)
2. K. Lorber et all, ACS Applied Materials & Interfaces, 2022, 14(28), 31862-31878
3. A. Upadhye et all, Catalysis Science & Technology, 2015, 5(5), 2590-2601
4. P. Ebrahimi et all, International Journal of Hydrogen Energy, 2022, 47(97), 41259-41267

Acknowledgements

Slovenian Research and Innovation Agency (ARIS) is acknowledged for funding via projects N2-0265 and P1-0418. Additionally, prof. dr. Nataša Novak Tušar is acknowledged for help and support.

SILCO Project: Waste-derived SILica-based porous solids for Carbon diOxide capture, storage and re-use catalytic technology

Lidia Castoldi[1], Cinzia Cristiani[*,2], Barbara Di Credico[3], Matteo Di Virgilio[2], Elisabetta Finocchio[*,4], Luca Lietti[1], Sergio Molina-Ramírez[2], Roberto Scotti[3], Lorenzo Vigano'[3]

[1]*Dipartimento di Energia (Laboratory of Catalysis and Catalytic Processes), Politecnico di Milano (POLIMI), Via la Masa 34, Milano, Italy.*

[2]*Dipartimento di Chimica, Materiali e Ingegneria Chimica Giulio Natta, Politecnico di Milano (POLIMI), Piazza Leonardo Da Vinci 32, Milano, Italy.*

[3]*Dipartimento di Scienza dei Materiali, Università Milano-Bicocca (UNIMIB), Piazza dell'Ateneo Nuovo, 1, Milano, Italy.*

[4]*Dipartimento di Ingegneria Civile, Chimica e Ambientale, Università di Genova (UNIGE), Via all'Opera Pia 15, Genova, Italy.*

*cinzia.cristiani@polimi.it; elisabetta.finocchio@unige.it

Significance and Relevance.

SILCO Project exhibits the potential to address both environmental and industrial challenges through innovative resource utilization. By transforming a hazardous industrial by-product hexafluorosilicic acid (FSA) into high-value silica, it advances the circular economy by converting waste into functional porous support for adsorption and heterogeneous catalysis applications. Waste-derived Silica produced as such, showing tunable porosity and surface area, are functionalized and tested as Dual-Function Materials (DFMs). DFMs integrate CO_2 adsorption and catalytic methanation functionalities, contributing to decarbonization strategies by enabling CO_2 capture and conversion into renewable methane, thus offering a sustainable and economically viable solution for CO_2 mitigation.

Preferred and 2nd choice for the topic: CO_2 Utilization and Recycling

Preferred presentation: Poster

Introduction and Motivations

Carbon dioxide remains one of the major responsible for the ongoing climate change, and the need to take urgent action to face this threat has motivated the scientific community efforts to develop efficient and cost-effective decarbonization strategies such as CO_2 Capture, Storage and Utilization (CCSU) systems. Among various technologies that have been developed to capture CO_2, adsorption and conversion by solid porous materials and catalysts is presented as a promising sustainable solution[1]. On the other side, there is a growing focus on developing sustainable processes that promote resource efficiency, prevent waste generation, and encourage the re-utilization of industrial waste by-products. Indeed, a hazardous by-product of aluminum fluoride and hydrofluoric acid industrial production is hexafluorosilicic acid (FSA, H_2SiF_6). FSA, as a co-product with limited applications, could be recovered and reused as a silicon-source for the production of silica with defined morphological and structural properties for catalytic support or sorbent applications.

In this frame, SILCO Project (PRIN2022PNRR-P2022SZANL) aims to integrate a zero-waste, innovative, and sustainable technological solution to use FSA for the production of silica. The integration deals with the modification of the waste-derived silica recovering process to produce morphologically controlled SiO_2 supports, which would be functionalized for application in sorbent (CCSU) and/or catalytic (green-fuel production) routes (Fig. 1). Among the different CO_2 hydrogenation strategies, the catalytic route to renewable methane through Sabatier reaction ($CO_2+4H_2 \rightarrow CH_4+2H_2O$) is favorable due to its high efficiency. With all these concepts, Dual Functions Materials (DFM)[2] based technology, acting as both as solid adsorbents for capture CO_2 and as catalysts for fuel production upon H_2 exposure, is promising. DFMs operate in cyclic alternating conditions, schematized in Fig. 2: firstly, the material is exposed to CO_2-containing gas stream until saturation (carbon capture function due to alkaline and/or earth-alkaline catalytic material functionalization) and, secondly, a regeneration phase is carried out exposing the DFM to a H_2 stream to convert $CO_2^{adsorbed}$ into CH_4 (hydrogenation function typically exploited by the incorporation of Ru or Ni). In literature, successful DFM consist of Ru-dispersed and Alkaline-(-earth)doped Al_2O_3-supported materials[3].

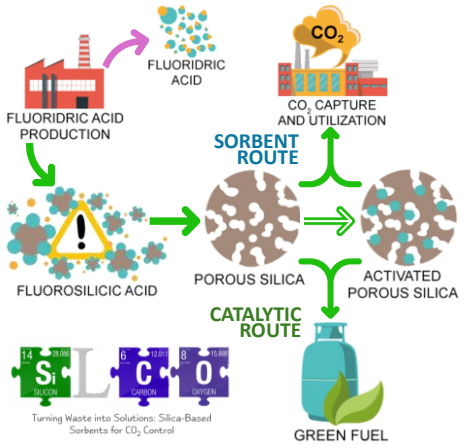


Figure 1. SILCO Project strategic development.

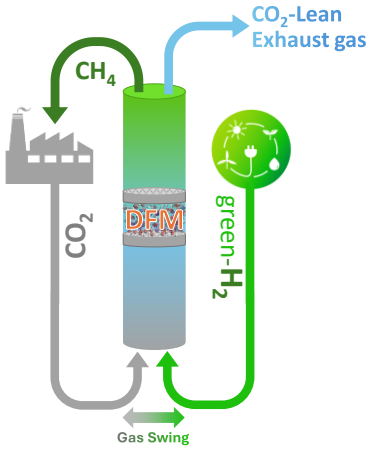


Figure 2. Schematic representation of alternating cycling condition process.

Results and discussion

Silica supports of controlled morphology, size, and porous structure, are synthesized in the presence of templates such as PEG, CTAB, and Pluronic-P123 and have been deeply characterized by FT IR spectroscopy, microscopies (SEM-EDX, HR-TEM-EDX), N_2-sorptometry, XRD, XPS, CO_2-TPD, inter alia. Acidity and surface properties have been also studied and compared to reference commercial materials. The supports will be then impregnated incorporating Ru (0.5% wt), and different Alkaline(-earth) oxides (i.e. Ba, Ca, K)[3]. The same preparation method has been used to obtain reference catalysts based on commercial SiO_2. FT-IR superficial characterization shows in case the presence of exposed silanol groups. Preliminary results obtained during the reduction of CO_2 with H_2, show that the CO_2 conversion over Ru-Ba catalysts does not depend on the support (Al_2O_3 or SiO_2); moreover, Ru-Ba/SiO_2 presents higher selectivity towards methane in respect of Ru-Ba/Al_2O_3 with the same composition (Fig. 3A,B).

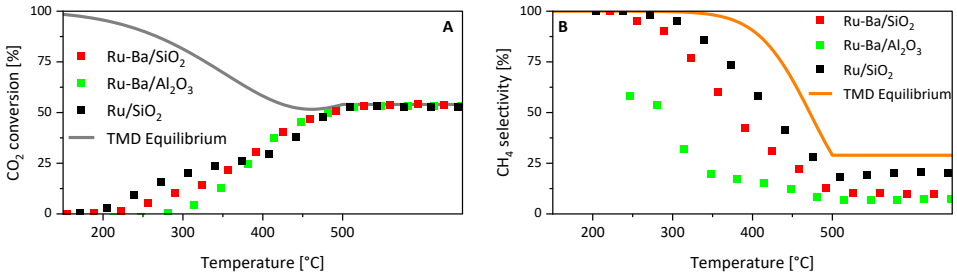


Figure 3. Results of TPR experiment: temperature ramp (from RT to 500°C @10°C/min) in CO_2 (1% v/v) + H_2 (4% v/v) balance He; A) CO_2 conversion; B) CH_4 selectivity.

Ru(0.5% wt)-Ba(16% wt)/SiO_2 has also been tested both in the adsorption of CO_2 and in its subsequent reduction. The catalyst at 150°C is able to adsorb near 230 µmol/g_{cat}, while during the reduction with H_2 only 63 µmol/g_{cat} of CH_4 are produced. This suggests that some carbonates remain on the surface that doesn't participate to the methanation reaction.

References

1. M. Sai, D. Ponnamma, K. Kumar, B. Kumar, A. Abdullah, *RSC Advances* **2021**, 11, 12658-12681.
2. M. Duyar, M. Arellano, R. Farrauto, *Applied Catalysis B: Environmental* **2015**, 168-169, 370-376.
3. A. Porta, R. Matarrese, C. Visconti, L. Lietti, *Energy&Fuels* **2023**, 37, 7280-7290.
4. www.silco.polimi.it

Acknowledgements

Authors acknowledge financial support of PRIN2022 PNRR SILCO (n. P2022SZANL) Project from the Italian Ministry of University and Research (MUR).

TiO_2/QDs nanocomposites for sustainable reactions: synthesis and characterization

Francesca S. FREYRIA[1], , Najeebullah CHANNA[1], Francesco PELLEGRINO[2], Jenny G. VITILLO,[3] Nicoletta DI TARANTO[4], Michele Bucchieri[1,5], Nicola BLANGETTI[1], Barbara BONELLI[1]

[1]1*Department of Applied Science and Technology and INSTM-Unit of Torino Politecnico, Corso Duca degli Abruzzi 24, Politecnico di Torino,10129 Torino, Italy*

[2] *Department of Chemistry, University of Torino, via Giuria 5, 10125 Torino, Italy*

[3] *Department of Science and High Technology and INSTM, Università degli Studi dell'Insubria, Via Valleggio 9, I-22100 Como, Italy*

[4]*Department of Chemistry, Università degli Studi di Bari Aldo Moro, 70125 Bari, Italy*

[5]*Departement of Chemistry, Biology and Biotechnologies- Università degli Studi di Perugia*

** e-mail francesca.freyria@polito.it*

Significance and Relevance

Sunlight reaching Earth each hour could meet global annual energy needs if were captured and stored affordably. Drawing inspiration from nature, this study investigates TiO_2 polymorphs enhanced with heavy-metal-free quantum dots (QDs) for two sustainable reactions: CO_2 reduction to solar fuels and biomass valorization. By coupling TiO_2, a well-studied photocatalyst, with non- toxic QDs, known for their excellent optoelectronic properties to harvest and deliver solar energy, this research aims to explore potential photocatalytic synergies between these nanoscale semiconductors. Preliminary experimental and modeling results indicate that selectivity and yield vary depending on the TiO_2 polymorphic type and QD concentration.

Preferred and 2nd choice for the topic: Photocatalysis and photoelectrocatalytic approaches, solar energy utilization

Green chemistry and biomass transformation, renewable resources conversion

Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster) Oral preferred or Short Oral

Introduction and Motivations

In recent decades, the twin challenges of climate change and increasing energy demands have become critical global issues. TiO_2, known for its low toxicity and affordability, is widely used as a photocatalyst to exploit solar energy for sustainable chemical reactions. Its main drawback is its large band gap which prevents it from absorbing photons in the visible range. To address this limitation, this study explores both the presence of different TiO_2 crystalline phases—anatase, rutile, and brookite—and the coupling with copper-based quantum dots that emit in the NIR range, to enhance light absorption and photocatalytic performance.[1]

Materials and Methods

TiO_2/$CuInS_2$ nanocomposites (TiO_2/CIS) were obtained at low temperatures without the use of template. Different titanium precursors, such as titanium tetrachloride and titanium tetraisopropoxide[2,3], were used to synthesize nanometric TiO_2.[4] Sodium oxalate and sodium lactate, as chelating agents, and urea, as in situ OH^- source, were added to tune the polymorphs percentages. $CuInS_2$ quantum dots were synthesized through one-pot synthesis method in inert atmosphere.[5] The two nanometric semiconductors were coupled in a controlled atmosphere at different temperatures.[3] Characterization of the studied nanomaterials has involved either theoretical calculations or experimental techniques such as X-ray powder diffraction (XRPD), quantitative phase analysis via Rietveld refinement, diffuse reflectance (DR) UV-Vis spectroscopy, N_2 adsorption/desorption, ζ-potential measurement for electrophoretic mobility in water, X-ray photoelectron spectroscopy (XPS), and electron microscopy. Photocatalytic performance assessment has been conducted under simulated sunlight at 1 Sun intensity (100 mW/cm^2).

Results and Discussion

By adjusting the chelating agents, aging time, and calcination temperature, we successfully controlled the quantity of polymorphs, allowing us to produce either single-phase or multiphase nanoscale TiO_2. These powders were coupled with $CuInS_2$ quantum dots (CIS-QDs) to enhance their photocatalytic activity. The influence of homo-(among the different TiO_2 polymorphs)[6] and hetero-junctions (between TiO_2 and CIS QDs) in the photocatalytic performance of the nanocomposites has been investigated through experimental techniques coupled with Kohn-Sham density functional calculations. KS-DFT calculations were used to model the different surfaces of the titania polymorphs to quantify their influence on the work function. We have been testing these nanocomposites for two sustainable reactions: i) CO_2 conversion in solar fuels; ii) lignin conversion into fragrances. Preliminary chromatographic analysis for CO_2 reduction revealed different amounts of C_1 and C_{2+} products, depending on the types of polymorphs present in the nanocomposite with CIS QDs. Furthermore, TiO_2/CIS nanocomposites appear to catalyze the conversion of dihydroeugenol to vanillin.

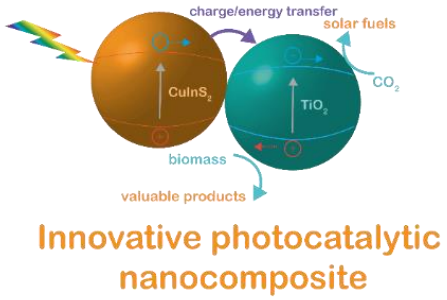


Figure 1 Sketch of the nanocomposite

References

(1) Freyria, F. S. ; Colloidal Semiconductor Nanocrystals for Artificial Photosynthesis. In *Nanostructured Catalysts for Environmental Applications*; Piumetti, M., Bensaid, S., Eds.; Springer International Publishing, 2021; pp 214–248. https://doi.org/10.1007/978-3-030-58934-9.

(2) Mutuma, B. K.; Shao, G. N.; Kim, W. D.; Kim, H. T. Sol-Gel Synthesis of Mesoporous Anatase-Brookite and Anatase-Brookite-Rutile TiO2 Nanoparticles and Their Photocatalytic Properties. *J Colloid Interface Sci* **2015**, *442*, 1–7. https://doi.org/10.1016/j.jcis.2014.11.060.

(3) Shen, F.; Que, W.; Liao, Y.; Yin, X. Photocatalytic Activity of TiO 2 Nanoparticles Sensitized by CuInS 2 Quantum Dots. *Ind Eng Chem Res* **2011**, *50* (15), 9131–9137. https://doi.org/10.1021/ie2007467.

(4) Freyria, F. S.; Blangetti, N.; Esposito, S.; Nasi, R.; Armandi, M.; Annelio, V.; Bonelli, B. Effects of the Brookite Phase on the Properties of Different Nanostructured TiO2 Phases Photocatalytically Active Towards the Degradation of N-Phenylurea. *ChemistryOpen* **2020**, 903–912. https://doi.org/10.1002/open.202000127.

(5) Li, L.; Pandey, A.; Werder, D. J.; Khanal, B. P.; Pietryga, J. M.; Klimov, V. I. Efficient Synthesis of Highly Luminescent Copper Indium Sulfide-Based Core/Shell Nanocrystals with Surprisingly Long-Lived Emission. *J Am Chem Soc* **2011**, *133* (5), 1176–1179. https://doi.org/10.1021/ja108261h.

(6) Xu, F.; Zhang, J.; Zhu, B.; Yu, J.; Xu, J. CuInS2 Sensitized TiO_2 Hybrid Nanofibers for Improved Photocatalytic CO2 Reduction. *Appl Catal B* **2018**, *230*, 194–202. https://doi.org/10.1016/j.apcatb.2018.02.042.

Acknowledgements

This study was carried out within the « GREEN UP: GREENER NANOMATERIALS FOR UPCONVERSION IN PHOTOCATALYTIC APPLICATIONS» project –funded by the Ministero dell'Università e della Ricerca –within the PRIN 2022 program (D.D.104 -02/02/2022) funded by the European Union - Next Generation EU. This manuscript reflects only the authors' views and opinions and the Ministry cannot be considered responsible for them".

Agritech National Research Center and received funding from the European Union Next-GenerationEU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) – MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.4 – D.D. 1032 17/06/2022, CN00000022). This manuscript reflects only the authors' views and opinions, neither the European Union nor the European Commission can be considered responsible for them.

The role of vanadium in silica-supported Ru catalysts for enhanced CO_2 methanation

Plaifa HONGMANOROM[1], Damien P. DEBECKER[*,1]
[1]*Institute of Condensed Matter and Nanoscience, UCLouvain, Place Louis Pasteur 1, Louvain-La-Neuve, Belgium.*
** damien.debecker@uclouvain.be*

Significance and Relevance

We report the first investigation into the promotional effect of vanadium on CO_2 methanation performance of Ru catalysts. This study revealed that V_2O_5 plays a beneficial role in stabilizing Ru nanoparticles and preventing their aggregation. Furthermore, hydrogen spillover from Ru during H_2 reduction and CO_2 hydrogenation promotes V_2O_5 reduction, generating oxygen vacancies and thereby facilitating electron transfer to interfacial Ru sites. This enhances CO_2 activation and CO adsorption on electronically modified Ru sites and interfacial Ru sites, significantly boosting methanation activity.

Preferred topic and 2nd choice for the topic: "Fundamental advances in understanding catalysis" and "CO_2 utilization and recycling"
Preferred presentation: Oral only

Introduction and Motivations

Converting CO_2 with green H_2 to produce CH_4 (CO_2 methanation) is a promising strategy to mitigate anthropogenic CO_2 emission while utilizing surplus green electricity (Power-to-Gas scenario).[1, 2] The promoting effects of alkali, alkali earth and lanthanide metals on Ru-based methanation catalysts have been extensively studied.[3, 4] However, little is known about the influence of transition metals – particularly vanadium – on the CO_2 methanation activity and selectivity of Ru catalysts.

Materials and Methods

The V-promoted silica materials were prepared via the aerosol-assisted sol-gel process. Tetraethyl orthosilicate, vanadium triisopropoxide, tetrapropylammonium hydroxide, and F127 surfactant were vigorously mixed to prepare the precursor solution, which was then atomized into small droplets and carried by air through the drying chamber. The dried powder was calcined at 550 °C. The loading of V was varied (x%V-SiO_2 where x = 4, 8, 12 and 16 mol%). To prepare Ru-based catalysts, the support materials were impregnated with RuO_2 nanoparticles (nominal 2 wt% Ru), which were pre-synthesized from the reaction between $RuCl_3$ and H_2O_2, and calcined at 450 °C.

Results and Discussion

An increase in V loading to 16% leads to a significant reduction in the specific surface area, from 492 m^2/g for Ru/SiO_2 to 34 m^2/g for Ru/16%V-SiO_2. Additionally, the morphology change is evident in Figure 1: Ru/SiO_2 catalyst exhibits a spherical morphology with mesopores, while Ru/16%V-SiO_2 catalyst shows an irregular shape with macropores. These changes are attributed to the formation of V_2O_5 crystallites in Ru/16%V-SiO_2, in accordance with the DRUV-vis and XRD results. Despite the decreased specific surface area, the catalytic activity of Ru/16%V-SiO_2 is markedly improved. Its methanation rate at 250 °C (168 $\mu mol_{\%\&}\ g_{)*}^{+,}\ s^{+,}$) is ca. 7-fold higher than that of Ru/SiO_2 (24 $\mu mol_{\%\&}\ g_{)*}^{+,}\ s^{+,}$), indicating that high surface area is not the determining factor for these catalysts. Instead, V_2O_5 helps stabilize Ru nanoparticles and prevent their aggregation, unlike in the case of Ru/SiO_2 catalyst, as illustrated in Figure 1. Furthermore, chemical and electronic modifications during H_2 reduction and CO_2 hydrogenation could positively influence the catalytic activity. The H_2-TPR profile of Ru/16%V-SiO_2 suggests the formation of Ru-V interaction, where hydrogen spillover from Ru facilitates further reduction of V_2O_5. Consistently, the band in the 300-500 nm region in Figure 2(a), corresponding to O^{2-}–V^{5+} charge transfer, decreases upon H_2 reduction and especially during reaction at 300 °C, indicating a decreased amount of V^{5+}. Simultaneously, a weak broad band emerges in the 500-700 nm region, attributed to the d-d transition of V^{4+} and/or V^{3+} species. The reduction of V^{5+} to V^{4+} or V^{3+} during exposure to H_2 or reactant mixture could generate oxygen vacancies, commonly

regarded as a source of electron carrier. This chemical modification by oxygen-vacancy formation could lead to electronic modification of Ru sites, which affects the adsorption of key CO intermediates, as observed in the in-situ DRIFTS spectra during CO_2 methanation at 300 °C (Figure 2(b)). For Ru/16%V-SiO_2 catalyst, alongside linear CO adsorption on metallic Ru (Ru-CO at 2055-1995 cm^{-1}), V_2O_5 could promote bridge CO adsorption at the metal-support interface (Ru_{if}-CO at 1971 cm^{-1}) and linear CO adsorption on electronically modified Ru sites (2074 cm^{-1}). Promotion of CO_2 activation and CO adsorption on these active sites may facilitate electron back-donation to the adsorbed CO, weakening C-O bonds for further hydrogenation towards CH_4 formation.

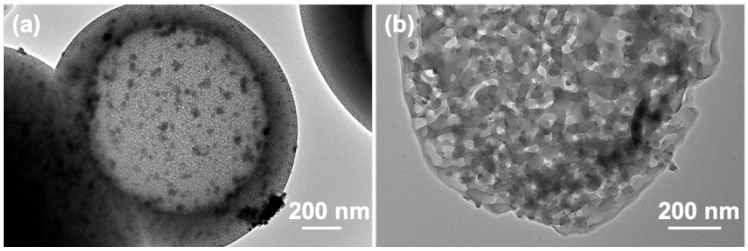


Figure 1. TEM images of (a) Ru/SiO_2 and (b) Ru/16%V-SiO_2 catalysts.

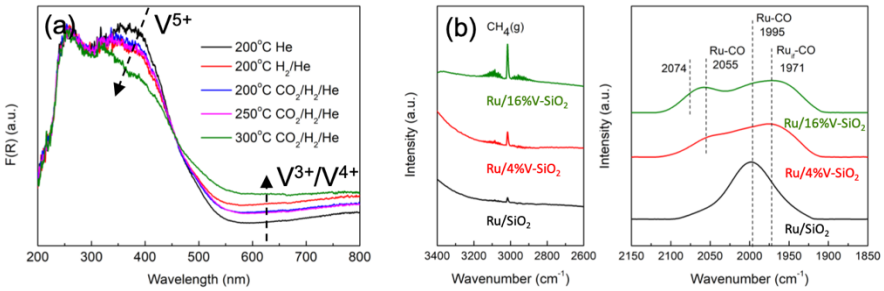


Figure 2. (a) In-situ DRUV-Vis spectra of Ru/16%V-SiO_2. (b) In-situ DRIFTS spectra during CO_2 methanation at 300 °C after 30 mins over Ru/SiO_2, Ru/4%V-SiO_2, and Ru/16%V-SiO_2 catalysts.

The CO_2 methanation activity of Ru/SiO_2 catalyst is significantly enhanced by the addition of vanadium promoter. The presence of V_2O_5 not only stabilizes Ru nanoparticles and prevents their aggregation but also provides the interaction between Ru and O-vacancies, facilitating electron transfer to interfacial Ru sites during H_2 reduction and CO_2 hydrogenation. This promotes CO_2 activation and CO adsorption on these sites, thereby improving catalytic activity in CO_2 methanation. This study enhances the understanding of the promoting effect of vanadium on CO_2 methanation. The potential of this vanadium promoter strategy could be further explored for other catalytic systems or reactions beyond CO_2 hydrogenation to CH_4.

References

1. J. Ashok, S. Pati, P. Hongmanorom, Z. Tianxi, C. Junmei, S. Kawi, *Catal. Today* **2020**, *356*, 471.
2. M.M.F. Hasan, L.M. Rossi, D.P. Debecker, K.C. Leonard, Z. Li, B.C.E. Makhubela, C. Zhao, A. Kleij, *ACS Sustainable Chem. Eng.* **2021**, *9*, 12427.
3. A. Petala, P. Panagiotopoulou, *Appl. Catal., B* **2018**, *224*, 919.
4. M. Gao, J. Zhang, P. Zhu, X. Liu, Z. Zheng, *Appl. Catal., B* **2022**, *314*, 121476.

Acknowledgements

This work was supported by the Southeast Asia-Europe Joint Funding Scheme for Research and Innovation (project PINT-MULTI/BEJ-R.8001.21).

Novel Hybrid Nanocomposites based on Au Nanoparticles Decorated Soot Carbon Nanoparticles for Electroanalytical Sensors

C. Ingrosso[1,*], F. Migliorini[2], W. Aidli[3], S. Dicorato[4], P. S. Sfragano[5], F. Spatafora[5], G. V. Bianco[4], V. Pifferi[3], M. Striccoli[1], M. Longhi[3], G. Cappelletti[3], M. L. Curri[1,6], I. Palchetti[5], L. Falciola[3]

[1]*CNR-IPCF S.S. Bari, c/o Dept. of Chemistry, Università degli Studi di Bari, via Orabona 4, 70126 Bari, Italy*

[2]*CNR-ICMATE S.S. Milano, Via Cozzi 53, 20125 Milano, Italy*

[3]*Dept. of Chemistry, Università degli Studi di Milano, via Golgi 19, 20133 Milano, Italy*

[4]*CNR-NANOTEC Sez. Bari, c/o Dept. of Chemistry, Università degli Studi di Bari, Via Orabona 4, 70126 Bari, Italy*

[5]*Dept. of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy*

[6]*Dept. of Chemistry, Università degli Studi di Bari, Via Orabona 4, 70126 Bari, Italy*

**email corresponding: chiara.ingrosso@cnr.it*

Significance and Relevance

Secondary raw materials such as soot carbon nanoparticles (NPs) were decorated with Au NPs by sustainable chemical colloidal approaches, resulting in original hybrid nanocomposites. The structural, spectroscopic, morphological and electrochemical properties of the novel nanocomposites were characterized, and their electroanalytical properties were tested in the detection of H_2O_2 and diclofenac (DFC) drug.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Soot carbon NPs, a by-product from incomplete hydrocarbon combustion, have garnered significant attention due to their adverse effects on climate, environment and human health [1]. However, their unique properties, such as a high surface to volume ratio, excellent electrical conductivity and remarkable thermal stability, have prompted interest in their use as a cost-effective graphitic alternative to commercial graphene derivatives. This potential upcycling into high added value nanocomposites offers a sustainable pathway for innovation in materials science [2]. Among various approaches, decorating soot NPs with Au NPs using solution-based chemical approaches, a strategy that has never been explored so far, can be effective, yielding hybrid materials with enhanced surface area, electrical conductivity and electrocatalytic performance. While extensive research exists on similar hybridization with carbon nanotubes, carbon black and graphene derivatives [3], very few studies have explored the decoration of soot carbon NPs with inorganic NPs [2]. In this work, a sustainable colloidal chemical approach was implemented to decorate soot carbon NPs with Au NPs, for the detection of H_2O_2 and DFC, a pharmaceutical water contaminant with serious human health and environmental concerns.

Results and Discussion

Soot carbon NPs were synthesized using a nitrogen-quenched ethylene diffusion flame, producing graphitic NPs of tens of nm in size, which formed fractal-like aggregates (Figure 1A). To graft oxygen-based functionalities at their surface, the soot NPs were treated with nitric acid under reflux conditions. This treatment preserved their morphology and graphitic properties, while grafting carbonyl and carboxylated groups (data not shown), which acted as coordinating sites for the *in situ* synthesis of Au NPs. Two methods were used to reduce the Au precursor ($HAuCl_4 \times 3H_2O$) onto the soot NPs: i. spontaneous galvanic displacement (Figure 1B), and ii. citrate assisted reduction (using $C_6H_5O_7Na_3 \times 2H_2O$) (Figure 1C). The citrate method was optimized by systematically varying the

citrate:Au precursor molar ratio and soot NPs:Au precursor w/w, and concomitantly investigating morphology of the resulting hybrid nanostructures. The Au NPs heteronucleated and grew on the oxygen-functionalized sites, with higher coating density achieved via citrate reduction, leading to the formation of an Au aerogel [4] supported on the graphitic carbon scaffold (Figure 1C). The soot NPs were characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), before and after decoration with the Au NPs. The CV results indicated an increase in the $Fe(CN)_6^{3-/4-}$ redox peaks compared to those observed at the bare SPCE electrode, and EIS data revealed a significant enhancement in the electrocatalytic activity and faster electron transfer kinetics at the electrodes modified with the soot NPs and soot/Au NPs (data not shown), underscoring the potential of the developed materials for electroanalytical applications. Preliminary tests for H_2O_2 and DCF detection showed promising results. The soot NPs demonstrated an improvement of the electrode performance in H_2O_2 (Figure 1D) and DCF detection (Figure 1E), that further enhanced in the soot/Au NPs sample synthesized with citrate. For H_2O_2, a linear limit of detection of 71 µM (sensitivity of 0.28 µA/mM) was reached in the soot/Au NPs sample synthesized by spontaneous reduction of the Au precursor (Figure 1D). For DFC, a shift in its characteristic oxidation peak towards lower potentials was observed at both the soot/Au NPs modified electrodes (Figure 1 E). These findings underscore the potential of the soot/Au NPs hybrid nanocomposites in the development of enzymatic biosensors, for clinical diagnostics, oxidative stress assessment and electrocatalytic sensors.

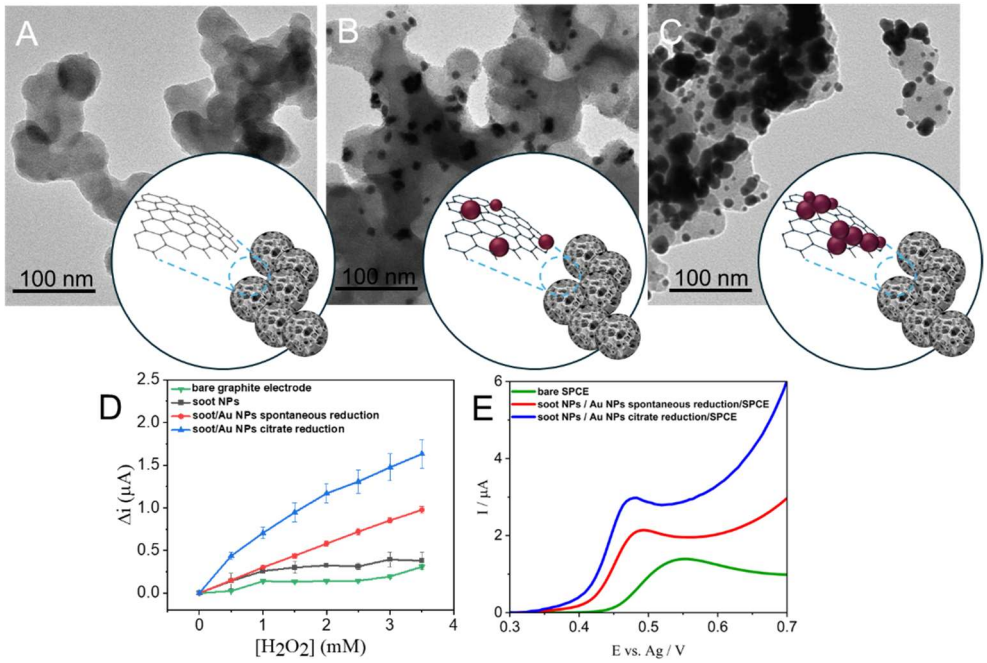


Figure 1. TEM micrographs of soot NPs A) pristine and decorated with Au NPs by spontaneous B) and citrated assisted reduction C). D) Chronoamperometric detection of H_2O_2 and E) DPV measurements of 10 µM DCF in 0.1M PBS at the investigated electrodes.

References

1. T.C. Bond, S. J. Doherty, D. W. Fahey et al. *J. Geophys. Res. D: Atmos.* **2013**, *118*, 5380
2. G. De Falco et al. *Proceedings of the Combustion Institute* **2024**, 40, 1–4, 105475
3. F. Vischio et al. *Biomaterials Advances* **2023**, 145, 213272
4. M. K. Kundu et al. *J. Mater. Chem. A, **2015**, 3, 23120*

Acknowledgements

The research was founded by Project PRIN 2022 UPSOOT cod. 2022SEYHXP from the Ministry of University and Research.

Biphasic Z-Scheme Photocatalytic System Using a Phase-Migrating Electron Mediator

Ren ITAGAKI[1,2], Akinobu Nakada[1*], Hajime Suzuki[1], Osamu Tomita[1], Ryu Abe[1*]
[1]*Kyoto University, Grad. Sch. of Eng., Kyoto daigaku-katsura, Nishikyo-ku, Kyoto, Japan.*
[2]*JSPS Research Fellow DC1, Kojimachi Business Center Building, 5-3-1 Kojimachi, Chiyoda-ku, Tokyo, Japan.*
** nakada@scl.kyoto-u.ac.jp (A.N.), ryu-abe@scl.kyoto-u.ac.jp (R.A.)*

Significance and Relevance

In recent years, photochemical molecular conversion reactions giving value added product have been attracting attention. Ideally, water should be used as an electron source to drive reductive photocatalytic reaction which only proceeds in organic solvent. In this study, we demonstrated a reductive photoredox catalysis coupled with water oxidation by separating the redox reaction fields with immiscible water/1,2-dichloroethane solutions and a ferrocenium/ferrocene phase-migrating electron mediator.

Preferred and 2nd choice for the topic: "Fundamental advances in understanding catalysis" or "Photocatalysis and photoelectrocatalytic approaches, solar energy utilization"……..
Preferred presentation: Poster……..

Introduction and Motivations

An artificial Z-scheme reaction system composed of two different photocatalysts[1] is a potential strategy for linking water oxidation with various reduction-based molecular transformations. We have developed a stepwise Z-scheme photocatalytic system using a biphasic solution using organic solvent that is immiscible with water.

Materials and Methods

The photocatalytic reductive coupling of benzyl bromide (Bn-Br) was performed by visible light irradiation of a biphasic solution of 1,2-dichloroethane (DCE) containing ferrocene (Fc; 5 or 10 mM), a photoredox catalyst (Ir-photosensitizer; 0.05 mM) and Bn-Br (50 mM) and H_2O exposure to visible-light ($\lambda > 400$ nm) under Ar atmosphere. The photocatalytic water oxidation was carried out in a suspension of a semiconductor photocatalyst (Bi-based oxyhalide) in an aqueous Fc^+ solution exposure to visible-light (λ = 430 nm) under Ar atmosphere. The evolved gases were analyzed by a O_2 sensor and the products in a liquid phase were analyzed by UV-vis absorption spectroscopy and HPLC.

Results and Discussion

Visible-light irradiation to a biphasic solution that composed of water and DCE solution containing a photoredox catalyst, Fc, and Bn-Br facilitated the reductive coupling of Bn-Br to dibenzyl (Bn_2; Figure 1a). Importantly, Fc^+, generated by photooxidation, migrates to the aqueous phase due to the drastic change in its partition coefficient compared to that of Fc.[2] On the other hand, visible-light irradiation to the same solution without water phase failed to generate any product (Figure 1b). This finding indicates that the phase migration of Fc^+ across a biphasic solution suppresses the unfavorable backward charge recombination, which enables the photoreduction of Bn-Br (Figure 1b).

The results on the coupled phase migration/photoinduced electron transfer prompted us to further investigate design principles in order to improve the efficiency of this photocatalytic reaction. The co-existence of anions can further modify the driving force of phase migration of Fc^+ depending on their hydrophilicity; the best photocatalytic activity was obtained with 100% yield for prepared Fc after continuous photocatalysis for 90 min in the presence of $NBu_4^+Br^-$ (red plots in Figure 1c). Thus, the liquid-liquid phase migration of the mediator results in effective charge separation, which leads to facilitate the reduction of Bn-Br in the DCE phase.[3]

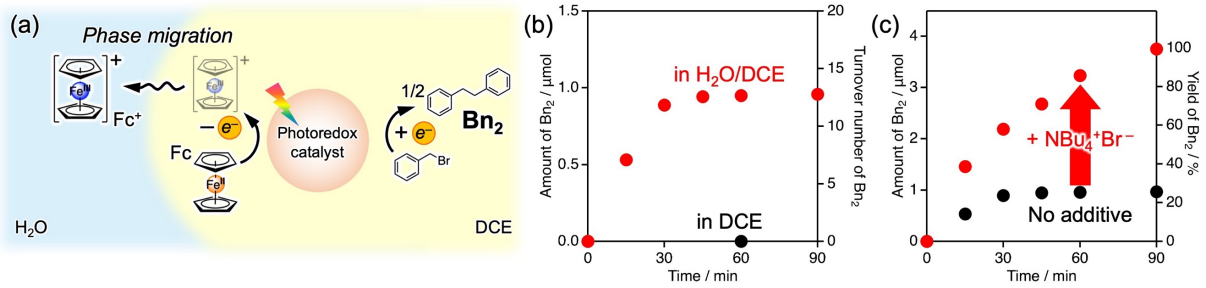


Figure 1 (a) Biphasic photocatalytic system for reductive coupling of Bn-Br designed in this study, time course of Bn_2 generation (b) in the DCE solution in the absence and presence of aqueous phase, and (c) in a H_2O/DCE (1:1, *v*/*v*) biphasic solution without additive (black plots) and in the presence of $NBu_4^+Br^-$ (red plots) under exposure to visible-light ($\lambda > 400$ nm).

On the other side, photogenerated Fc^+ can be utilized as an electron acceptor for photocatalytic water oxidation with a semiconductor photocatalyst in the aqueous phase (Figure 2b). In an aqueous solution, a semiconductor photocatalyst performed photocatalytic water oxidation with a Fc^+ electron acceptor which was generated after photocatalytic reduction of Bn-Br using Fc explained above, generating O_2 and Fc (Figure 2b). More importantly, the ratio of generated Bn_2 (5.0 μmol) and O_2 (2.5 μmol) satisfies the stoichiometry corresponding to the overall reaction (Figure 2b and c; Eq. 1).

Eventually, the Fc^+/Fc redox couple transports an electron by the photoredox induced liquid-liquid phase migration to achieve photoreduction of Bn-Br coupled with water oxidation (Eq. 1).

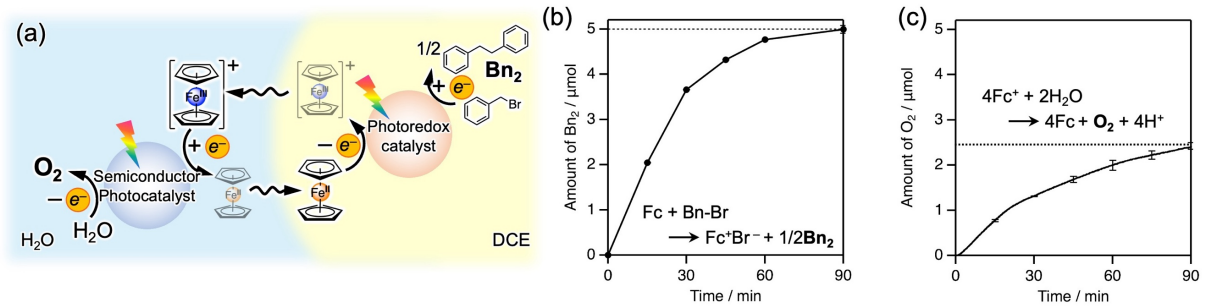
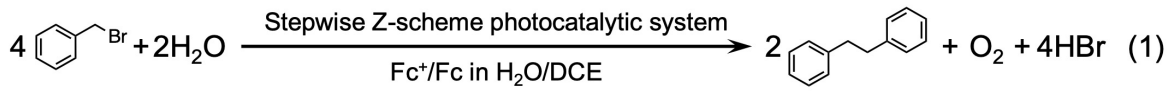


Figure 2 (a) Conceptual scheme of a biphasic Z-scheme photocatalytic system using Fc^+/Fc as a phase-migrating electron mediator. Time course of half reactions of (b) Bn_2 formation using photoredox catalyst and Fc as an electron donor in a H_2O/DCE (1:1, *v*/*v*) biphasic solution under exposure to visible-light (λ = 470 nm), and (b) O_2 evolution using photogenerated Fc^+ by Bn_2 production as an electron acceptor and a semiconductor photocatalyst under exposure to visible-light (λ = 430 nm) by a stepwise one. The dashed line shows the upper limit of Bn_2 and O_2 evolution expected from the amount of Fc added to these solutions.



References

1. R. Abe, J. Tang, *et al. Chem. Rev.* **2018**, *118*, 5201.
2. Henry. S. W., *et al. J. Am. Chem. Soc.* **2019**, *141*, 18091.
3. R. Itagaki, A. Nakada, *et al. Dalton Trans.* **2022**, *51*, 9467.

Acknowledgements

Grant-in-Aid for Scientific Research on Innovative Areas “Innovation for Light-Energy Conversion (I4LEC)” from MEXT (JP20H05113 and JP17H06439) and Grant-in-Aid for Young Scientists (22K14769)

Tribocatalytic Degradation of Chloramphenicol Using Eu-Doped ZnO Catalysts: A Sustainable Approach to Pharmaceutical Pollutant Removal

Dobrina IVANOVA[1], Bozhidar STEFANOV[2], Hristo KOLEV[3], Nina KANEVA[1]

[1]*Laboratory of Nanoparticle Science and Technology, Department of General and Inorganic Chemistry, Faculty of Chemistry and Pharmacy, University of Sofia, 1164 Sofia, Bulgaria*
[2]*Department of Chemistry, Faculty of Electronic Engineering and Technologies, Technical University of Sofia, 8 Kliment Ohridski Blvd, 1756 Sofia, Bulgaria*
[3]*Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., bl. 11, 1113 Sofia, Bulgaria*
** Dobrina.k.ivanova@gmail.com*

Significance and Relevance

The study demonstrated that Eu doping enhanced the tribocatalytic activity of ZnO for degrading chloramphenicol under mechanical agitation. Characterization by XPS confirmed successful incorporation of Eu, while SEM and EDS revealed uniform distribution and modified surface morphology. UV-Vis spectroscopy showed significant degradation efficiencies for all Eu-doped ZnO catalysts, with improvements over undoped ZnO. This work is novel as it highlights the role of rare-earth doping in tribocatalysis, offering an innovative, energy-efficient method for degrading pharmaceutical pollutants, a growing environmental concern.

Preferred and 2nd choice for the topic: Water treatment, Fundamental advances in understanding catalysis
Preferred presentation: Poster

Introduction and Motivations

Pharmaceutical pollutants, such as paracetamol and chloramphenicol, are emerging contaminants in water systems, posing significant risks to ecosystems and human health. Conventional water treatment methods often fail to degrade these persistent compounds effectively. Tribocatalysis, a novel approach leveraging mechanical energy to activate catalysts, offers an energy-efficient and sustainable solution. Zinc oxide (ZnO) is a promising catalyst due to its semiconductor properties, and rare-earth doping, such as europium (Eu), can enhance its activity. This study explores Eu-doped ZnO for tribocatalytic degradation, motivated by the need for innovative technologies to tackle pharmaceutical pollution.

Results and Discussion

Tribocatalysis has emerged as an innovative and sustainable approach for degrading organic pollutants in wastewater. This study investigates the tribocatalytic degradation of pharmaceutical contaminant chloramphenicol, using zinc oxide (ZnO) catalysts doped with europium (Eu) at concentrations of 1, 2, and 3 mol%. The catalysts were synthesized via the sol-gel method, ensuring uniform doping and optimal surface properties for catalytic performance.

The catalysts were characterized using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and Fourier-transform infrared spectroscopy (FTIR) to analyze their chemical composition, surface morphology, and elemental distribution.

The tribocatalytic degradation of the target pollutants was evaluated under mechanical agitation, and degradation efficiencies were determined using UV-Vis spectroscopy. The study revealed that Eu doping significantly influenced the tribocatalytic activity of ZnO by modifying its electronic structure and enhancing pollutant degradation.

This work demonstrates the potential of Eu-doped ZnO catalysts in addressing pharmaceutical contamination in water, emphasizing the role of tribocatalysis as an eco-friendly and effective water treatment technology.

Efficient search for acetic acid synthesis pathway based on the bond disconnection process on Rh surface and Rh/metal oxide interface

Kenshin CHISHIMA[1], Takumi MASUDA[1], Hiroshi SAMPEI[1], Koki SAEGUSA[1], Sakuya HATTORI[1], and Yasushi SEKINE[1]

[1] *Waseda University, Department of Applied Chemistry, 3-4-1, Okubo, Shinjuku-ku, Tokyo, Japan.*

** ysekine@waseda.jp*

Significance and Relevance

This study revealed that the Rh/*t*-ZrO_2 (101) interface promotes efficient acetic acid (CH_3COOH) synthesis by forming acetyl (CH_3CO) intermediate from Rh-bound CH_3 and CO. The C-O bond elongation occurs as Rh-CO interacts with Zr cations, significantly lowering the activation energy for the coupling between CO and CH_3 to 0.73 eV. These findings explain the experimentally observed C-O bond weakening and increased production of C_2 oxygenates on Rh-Zr oxide catalysts. By identifying this CO structure at the Rh-ZrO_2 interface, the study establishes a rational design framework for engineering catalytic interfaces to enhance acetic acid synthesis from syngas.

Preferred and 2nd choice for the topic:
Fundamental advances in understanding catalysis / CO_2 utilization and recycling
Preferred presentation: Poster

Introduction and Motivations

The structure of active sites for acetic acid production from C1 molecules, such as CO and CO_2, using rhodium-supported catalysts remains unclear. This study created Rh monometallic and Rh/metal oxide interface models to investigate the acetic acid synthesis pathways in each model.

Materials and Methods

All calculations for structural optimization were conducted using Matlantis (v.3.0.0), a general-purpose atomic simulator that performs calculations based on the PreFerred Potential (PFP), one of the neural network potentials (NNPs).[4] The convergence threshold of structure optimization was set to be 10^{-5} eV. The adsorption energy E_{ad} of each adsorbate on the catalyst surface model was calculated by the following equation (1).

$$_{\mathrm{ad}} = \ (\mathrm{adsorbate/surface}) - \ (\mathrm{surface}) - \ (\mathrm{adsorbate}) \qquad (1)$$

Where *E*(adsorbate/surface) and *E*(surface) are the total energy of the surface slab model with and without adsorbates, respectively. The *E*(adsorbate) is the total energy of each adsorbate, which was calculated with an adsorbate existing in a 20 Å cubic box. The Climbing Image Nudged Elastic Band (CI-NEB) method was performed to calculate the energy of the transition state during the bond disconnection process of the adsorbate.[5] The convergence threshold was set to be 0.005 eV, the number of images to 13, and the force constant to 0.05 eV $Å^{-1}$. Here, the activation energy $E_{a(c)}$ of the bond connection process was calculated from the following equation (2). E_{TS}, E_{FS} denote the energy of the transitional state and final state, respectively.

$$_{\mathrm{a(c)}} = \ _{\mathrm{TS}} - \ _{\mathrm{FS}} \qquad (2)$$

Results and Discussion

The reaction pathways involving processes characterized by smaller activation energies, $E_{a(c)}$ were thoroughly investigated based on the comprehensive analysis of the disconnection process. It was determined that at the Rh/*t*-ZrO_2(101) interface, the synthesis of acetic acid can proceed favorably on the point of kinetics through the formation of the acetyl structure (CH_3CO) from the interaction between Rh-CH_3 and Rh-CO species. This significant and intriguing finding is illustrated in Figure 1. Figure 1 (a) presents the detailed calculation model of the Rh/*t*-ZrO_2(101) interface, and (b) shows the energy diagram that was proposed by this investigation. Figures 1 (c) through (g) correspond to the visualized structures that were observed during the acetic acid synthesis pathway proposed in this study. As illustrated in Figure 1 (g), Rh-CO interacts with the Zr cations in the zirconia support *via* the oxygen atom in the adsorbed CO, which will be referred to henceforth as the CO_s structure (s means "support"). Notably, during this interaction, the length of the C-O bond is significantly elongated, leading to a substantial reduction in the activation energy of the CO insertion into CH_3 to 0.73 eV. These noteworthy and important results can provide a comprehensive explanation for the experimentally observed development of IR band structure that is originated from C-O stretching, particularly with the weakened C-O bond, and they also correlate closely with the increased production of C_2 oxygenates, including ethanol, acetaldehyde, and acetic acid, on catalysts that consist of both Rh and Zr oxides. Given these discussions, it is expected that the CO_s structure at the interface between Rh and ZrO_2 will play a crucial role in enhancing the efficiency of acetic acid synthesis from C_1 molecules, such as CO and CO_2, contributing significantly to future research in this area.

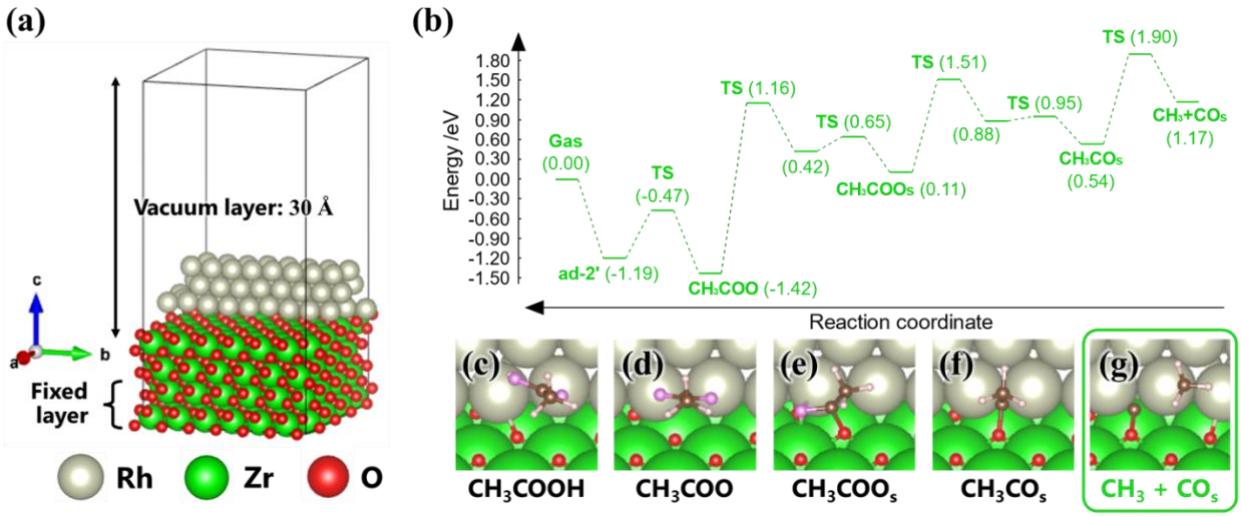


Figure 1 Rh/*t*-ZrO_2(101) model and energy diagram of acetic acid synthesis pathway.

References

1. A. Trunschke, H. Ewald, H. Miessner, S. Marengo, S. Martinengo, F. Pinna, and L. Zanderighi, *J. Mol. Catal.* **1992**, *74(1-3)*, 365-377.
2. A. L. Borer, C. Bronnimann, and R. Prins, *J. Catal.* **1994**, *145(2)*, 516-525.
3. L. Han, D. Mao, J. Yu, Q. Guo, and G. Lu, *Appl. Catal. A: Gen.* **2013**, *454(15)*, 81-87.
4. S. Takamoto, D. Okanohara, Q. J. Li, and J. Li, *J. Mater.* **2023**, *9*, 447-454.
5. D. Sheppard, P. Xiao, W. Chemelewski, D. D. Jonson, and G. Henkelman, *J. Chem. Phys.* **2012**, *136*, 074103.
6. W. M. H. Sachtler, and M. Ichikawa, *J. Phys. Chem.* **1986**, *90(20)*, 4752-4758.

Acknowledgements

The author acknowledges ENEOS for the use of Matlantis.

Theoretical Design of CeO_2-Based Materials for Enhanced RWGS-CL Performance

Koki SAEGUSA[1], Takuma HIGO[1], Shuhei ISHIZAKI[1], Sota KAKIHARA[1], Hiroshi SAMPEI[1], and Yasushi SEKINE[*,1]

[1] *Department of Applied Chemistry, Waseda University, 3-4-1, Okubo, Shinjuku, Tokyo, Japan.*

** ysekine@waseda.jp*

Significance and Relevance

Reverse water gas shift reaction via chemical looping (RWGS-CL) enables efficient CO_2 utilization through materials with high oxygen storage capacity. Through theoretical calculations, we predicted enhanced oxygen release capability in Pr-doped CeO_2, which achieving a higher reduction rate and increased redox capacity (>99% CO_2 conversion at 773 K) experimentally. *In-situ* XAFS measurements and theoretical calculations revealed that Ce-O-Pr interactions tune Ce valence states, leading to enhanced RWGS-CL performance. This study demonstrates the successful theory-driven development of $Ce_{0.67}Pr_{0.33}O_2$, achieving enhanced RWGS-CL performance.

Introduction and Motivations

CO_2 utilization under moderate conditions is essential for addressing environmental challenges. Among various approaches, the reverse water gas shift (RWGS) reaction has attracted widely[1]. The RWGS reaction is the equilibrium process that produces CO from CO_2 and H_2, as shown in equation (1).

$$_2 + \quad _2 \rightarrow \quad + \quad _2 \ , \ \Delta \ ^\circ_{298} \quad = 42.1 \qquad ^{-1} \tag{1}$$

However, the RWGS reaction faces several challenges. Due to its endothermic nature, it requires higher temperatures to achieve high CO_2 conversion. Additionally, equilibrium limitations, methanation side reactions, and product separation costs pose significant constraints.

To overcome these challenges, we focus on RWGS reaction via chemical looping (RWGS-CL)[2], which can separate the whole redox reaction into oxidation and reduction steps using the lattice oxygen from metal oxides (MO_x), as described in equation (2) and (3).

$$+ \quad _2 \rightarrow \quad _- + \quad _2 \tag{2}$$

$$_- + \quad _2 \rightarrow \quad + \tag{3}$$

By separation of reaction gas, RWGS-CL emerges as a promising process for CO_2 utilization under moderate conditions. Previous studies have investigated suitable materials for RWGS-CL, focusing on lattice oxygen release and refill capabilities in perovskite and spinel oxides. However, these materials still require temperatures exceeding 823 K[3,4]. Thus, developing materials with high oxygen storage capacity at lower temperatures is crucial for enhancing RWGS-CL performance.

In this study, we conducted the theory-driven screening of suitable material for RWGS-CL focusing on CeO_2-based materials. Also, we evaluated the experimental CO_2 conversion performance and uncovered the dominant factors through surface analysis, combining theoretical calculations with spectroscopic investigations. Our results demonstrate that material design based on theoretical calculations can provide valuable insights for developing novel oxygen carrier materials.

Materials and Methods

The theoretical material screening and other evaluations were carried out with Matlantis[5], an atomistic simulator of density functional theory calculations. All calculations used v4.0.0 of the PFP neural network potential[6] based on GGA-PBE functional. For material screening, CeO_2 (111) surface models with various cations ($Ce_{0.67}M_{0.33}O_2$: M=V, Cr, Mn, Y, Zr, Mo, Pr, Nd, Sm, Gd), which consists of (6×6) supercell with six O-Ce-O tri layers, were constructed and optimized. Dopant positions were determined by minimizing formation energies. Since oxygen vacancy formation ability significantly influences the reaction, each doped surface model with a lattice oxygen vacancy was also prepared, and their oxygen vacancy formation energies were evaluated. Moreover, $Ce_{0.67}M_{0.33}O_2$ (M=Cr, Mn, Y, Zr, Pr, Nd, Sm, Gd) samples were synthesized by citric acid complex polymerization, with calcination at 823 K for 10 h. The redox behavior was evaluated through isothermal RWGS-CL tests at 773 K using a thermogravimetric analyzer (TGA-50; Shimadzu Corp.), under 10vol% H_2 and 10vol% CO_2 flow for

reduction and oxidation steps. Additionally, XPS and XAFS measurement and Bader charge analysis were performed for uncovering the dominant factors of RWGS-CL using CeO_2-based materials.

Results and Discussion

From the theoretical material screening, we discovered that Pr-doped CeO_2 exhibits the lowest formation energy of oxygen vacancy among various dopants, indicating facilitated lattice oxygen release. Isothermal RWGS-CL tests validated our theoretical predictions, with $Ce_{0.67}Pr_{0.33}O_2$ achieving both the highest redox amount and 99% CO_2 conversion to CO (Fig. 1(a)). The Pr doping ratio change tests revealed that the oxygen vacancy formation energy decreases and the redox amount increases as the Pr doping ratio was increased (Fig. 1(b)). While these materials with larger doping ratios display some structural distortion in XRD measurements, they retain the fluorite structure of the pure CeO_2 throughout the reaction, which brings high stability across 10 RWGS-CL cycles.

To elucidate the redox mechanisms of $Ce_{0.67}Pr_{0.33}O_2$, theoretical charge analysis and *in-situ* XAFS measurement were conducted. Bader charge analysis result (Fig. 2(a)) revealed that two key trends: first, Ce atom charge intensifies with increasing Pr doping ratios; second, this charge diminishes during oxygen release, with $Ce_{0.67}Pr_{0.33}O_2$ demonstrating a more substantial decrease compared to pure CeO_2. Moreover, linear combination fitting of *in-situ* XAFS data (Fig. 2(b)) confirmed that more pronounced changes in Ce^{3+} fraction for $Ce_{0.67}Pr_{0.33}O_2$ relative to pure CeO_2 , supporting our theoretical charge analysis findings. These analyses established that Pr doping enhances Ce^{4+}/Ce^{3+} redox cycling throughout reaction steps. To distinguish between structural and electronic effects of Pr doping, we prepared a theoretical model replacing Pr with Ce while preserving the Pr-induced structural distortion. Notably, oxygen vacancy formation energy of prepared calculation model becomes the similar to that of the pure CeO_2, confirming that electronic structure modification through Pr doping, rather than structural distortion, predominantly drives the enhanced RWGS-CL performance of $Ce_{0.67}Pr_{0.33}O_2$.

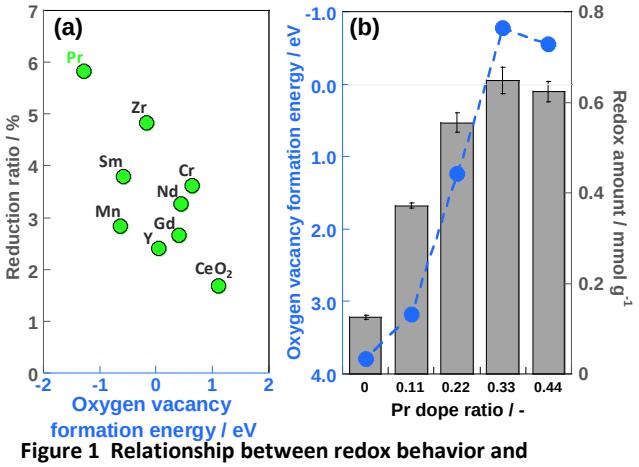


Figure 1 Relationship between redox behavior and oxygen vacancy formation energy on (a) dopant and (b) Pr doping ratio change tests.

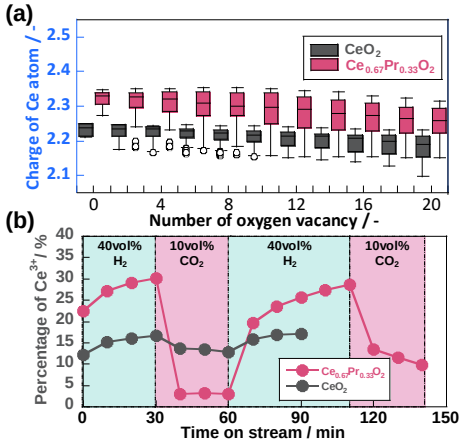


Figure 2 Ce charge analysis through reactions by (a) Bader charge analysis and (b) *in-situ* XAFS.

In conclusion, our theoretical screening identified Pr-doped CeO_2 as an optimal RWGS-CL material, demonstrating minimal oxygen vacancy formation energy and superior redox capacity. Bader charge analysis and *in-situ* XAFS revealed that Pr doping promotes Ce^{4+}/Ce^{3+} redox cycle because of tuning the electronic structure by Ce-O-Pr interactions. These findings establish electronic structure control by compositional engineering as a design strategy for optimizing RWGS-CL and related redox reactions.

References

1. Y.A. Daza *et al.*, *RSC Adv.* **2016**, *6*, 49675-49691.
2. V.V. Galvita *et al.*, *Ind. Eng. Chem. Res.* **2013**, *52*, 8416-8426.
3. Y. Qiu *et al.*, *J. Energy Chem.* **2020**, *46*, 123-132.
4. Y.A. Daza *et al.*, *Catal. Today* **2015**, *258*, 691-698.
5. Matlantis (https://matlantis.com/), software as a service style material discovery tool.
6. S. Takamoto *et al.*, *Nat. Commun.* **2022**, *13*, 2991.

CO_2 HYDROGENATION TO LIGHT OLEFINS OVER FE-BASED MIXED OXIDES DERIVED FROM LAYERED DOUBLE HYDROXIDES

Athanasia KOTSARIDOU[1,*], Antigoni MARGELLOU[1], Evridiki MANDELA[2], Michail KONSOLAKIS[3], Georgios MARNELLOS[4], Konstantinos TRIANTAFYLLIDIS[1]

[1]*Aristotle University of Thessaloniki, Department of Chemistry, Thessaloniki, Greece*

[2]*University of Western Macedonia, Department of Mechanical Engineering, Kozani, Greece*

[3]*Technical University of Crete, School of Production Engineering and Management, Chania, Greece*

[4]*Aristotle University of Thessaloniki, Department of Chemical Engineering, Thessaloniki, Greece*

** e-mail corresponding: nancykotsa7@gmail.com*

Significance and Relevance

This work provides useful insights on the catalytic CO_2 conversion towards light olefins over low-cost mixed oxides which can be easily produced in pilot scale. The conversion and the selectivity of light olefins can be controlled via the selection of appropriate metals combination.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling
Preferred presentation: Poster

Introduction and Motivations

Carbon dioxide can be captured and utilized towards the production of platform chemicals and fuels. Catalytic hydrogenation of carbon dioxide can lead to the formation of light olefins (C_2-$C_{4=}$) and has been recognized as a promising process compared to the traditional naphtha steam cracking. The hydrogenation of carbon dioxide can be proceeded via a two-step process: initially the carbon dioxide is converted to carbon monoxide via the reverse water-gas shift (RWGS) reaction and subsequently the CO is converted to light olefins via Fischer-Tropsch (FTS) reaction. This two step process results to low light hydrocarbons selectivity (58%) and thus research efforts have recently focused on the development of novel catalytic systems to enhance both the conversion and the selectivity towards light olefins. This work focused on the development of iron based mixed oxides derived from Layered Double Hydroxides (LDH) and their evaluation in the hydrogenation of CO_2 towards light olefins.

Materials and Methods

The catalysts were synthesized via co-precipitation followed by hydrothermal treatment. A wide variety of metals (Mg, Fe, Zn, Al, Co, Cu, Ni) with different ratios have been used in the synthesis of layered double hydroxides. The final mixed oxides were obtained via the calcination of LDH at 500°C for 3 h. All catalysts were characterized via various techniques (XRD, XPS, SEM, N_2-physisorption) to determine their structural and porous properties. The hydrogenation of CO_2 was performed at 350 °C and 20 bar under a stoichiometric feed ratio of H_2: CO_2=3:1 and WHSV=6000 ml/g/h.

Results and Discussion

Regarding the catalyst characterization, the as-received materials exhibit the hydrotalcite structure as confirmed via the XRD analysis. The calcined materials exhibit either the crystal structure of mixed oxides or the structure of spinels. Furthermore, the porous properties of the materials are strongly dependent on the metals' combination and ratios. The combination of metals and their ratio exhibit different catalytic activity in the CO_2 hydrogenation to light olefins. In general, Mg-based catalysts are more selective towards CO formation, while Cu and Co-based materials exhibited higher selectivity towards CH_4. Highest selectivity towards light olefins were observed with Zn-Fe-Al mixed oxides which exhibit CO_2 conversion in the range of 8-42%. The highest yield (10.6%) towards C_2-$C_{4=}$ olefins was observed for Zn-Fe-Al with $(Zn^{2+}+Fe^{2+})/Al^{3+}$=2.6 and 40 wt.% Fe, while the material without iron (Zn/Al=2) did not show significant catalytic activity, implying that iron has a key role in the reaction (Figure 1). Apart from iron content, iron valence also has a significant effect on light olefins yield. Partial substitution of Al^{3+} with Fe^{3+} ($Zn^{2+}/(Fe^{3+}+Al^{3+})$ = 2.2, 15 wt.% Fe) led to lower yield of light olefins, 4.7%,

proving that Fe^{2+} is more active than Fe^{3+}. Also, important parameters are the crystal structure and the porous properties of the materials. As a result, iron-based mixed oxides are promising catalysts for the conversion of CO_2 towards light olefins while optimization of iron amount and valence can enhance the conversion and the yield of olefins instead of methane, carbon monoxide and paraffins.

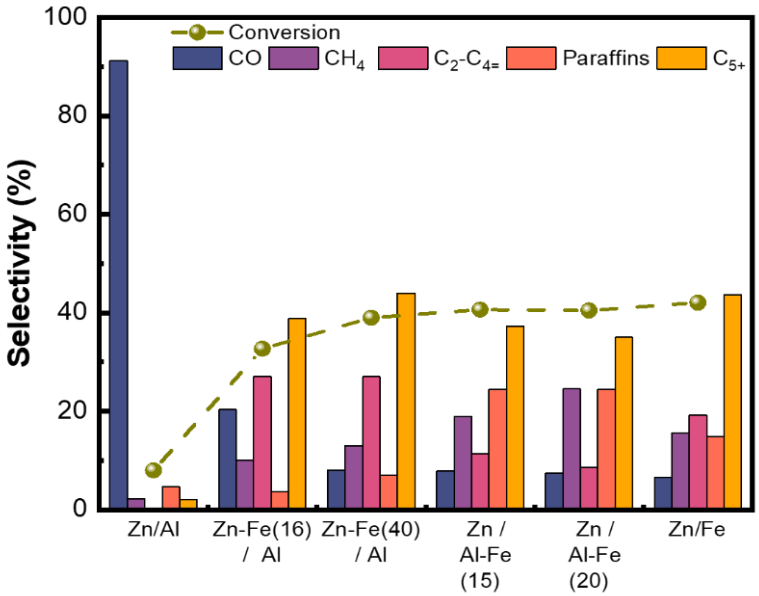


Figure 1. Conversion of CO_2 towards light olefins over Fe-based mixed oxides.

Acknowledgements

This research has been co-financed by the European Union NextGenerationEU under the call RESEARCH-CREATE-INNOVATE 16971 Recovery and Resilience Facility (project code: TAEDK-06169).

High-Throughput Optimization of Mo-Doped $BiVO_4$ Thin Films Using SPECM for Enhanced Photoelectrochemical Performance

Hyeon-Bin Lee[1,2], Jae-Cheol Park[1], Soe-Jin Jeong[1], Si-Yun Jeong[1], Jun-Seok Ha[2], Tae-Won Kim[*,1]
[1] *Energy & Nano Technology Group, Korea Institute of Industrials Technology*
6, Cheomdan-gwagiro 208-gil, Buk-ku, Gwangju, 61012, Republic of Korea.
[2] *Department of Chemical Engineering, Chonnam National University*
77, Yongbong, Buk-gu, Gwangju 500-757, Republic of Korea.
** e-mail corresponding: twkim90@kitech.re.kr*

Significance and Relevance

This study presents the successful optimization of molybdenum-doped BiVO4 thin films, achieving a significant enhancement in photocurrent density for water splitting applications. Using a combinatorial sputtering method, we identified optimal doping levels and conditions that reduce electron-hole recombination, extend light absorption, and improve structural stability. These results provide a scalable approach to developing efficient and durable photoanodes for solar-driven hydrogen production.

Preferred choice for the topic: Photocatalysis and photoelectrocatalytic approaches, solar energy utilization
2nd choice for the topic: H2 storage and transportation, green H2 production, hydrogen vectors
Preferred presentation: Poster

Introduction and Motivations

$BiVO_4$ is a promising material for photoelectrochemical (PEC) water splitting due to its suitable bandgap and stability. However, its performance is limited by high electron-hole recombination and low charge mobility.[1] Molybdenum (Mo) doping addresses these issues by modifying the band structure, improving light absorption, and enhancing charge transport.[2] This study explores the synthesis, optimization, and PEC performance of Mo-doped $BiVO_4$ thin films using combinatorial sputtering.

Materials and Methods

Mo-doped $BiVO_4$ thin films were fabricated using RF magnetron sputtering with a combinatorial approach to create a gradient of Mo doping concentrations across the samples. The films were deposited on FTO-coated glass substrates under controlled conditions. Two sputtering targets were used: a pure $BiVO_4$ target and a 10 at.% Mo-doped $BiVO_4$ target. During the deposition, the RF power for the pure $BiVO_4$ target was fixed at 200 W, while the RF power for the 10 at.% Mo-doped $BiVO_4$ target was varied between 0 W and 200 W to produce a series of samples with varying Mo doping concentrations. This combinatorial sputtering method generated thin film libraries with doping gradients. To evaluate the photoelectrochemical (PEC) properties, Scanning Photoelectrochemical Microscopy (SPECM) was employed, enabling high-throughput analysis of local photocurrent responses across the doping gradient. Structural and optical characterizations were performed using SEM, XRD, and UV-Vis spectroscopy to correlate the film properties with their PEC performance.

Results and Discussion

The SPECM analysis of the combinatorial thin film libraries enabled the rapid identification of the optimal Mo doping concentration. At an RF power of 100 W for the Mo-doped target, the photocurrent density reached a maximum of 0.8–1.0 mA/cm² at 1.23 V vs. RHE. This corresponded to an optimal doping level of 2–3 at.%. The localized PEC measurements revealed significant suppression of electron-hole recombination and enhanced charge carrier mobility in the optimally doped regions. XRD patterns showed the formation of well-defined crystalline structures with reduced defect densities, while UV-Vis spectroscopy indicated an extended light absorption range due to bandgap narrowing. SEM mapping confirmed uniform distribution of Mo within the optimized thin films. Figure 1 highlights the

relationship between RF power and photocurrent density, demonstrating the efficiency of the SPECM-driven optimization process.

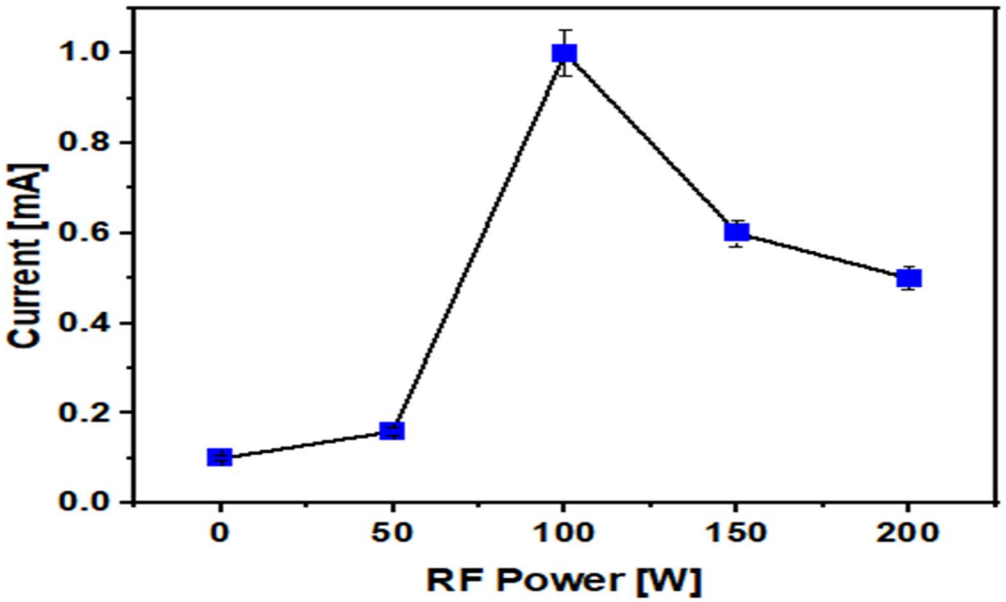


Figure 1. Relationship between RF power for Mo-doped $BiVO_4$ target and photocurrent density measured by SPECM at 1.23 V vs. RHE

References

1. Wang, S., Liu, B., Wang, X. et al. Nanoporous $MoO_{3-x}/BiVO_4$ photoanodes promoting charge separation for efficient photoelectrochemical water splitting. *Nano Res.* **2022**, 15, 7026–7033.
2. Martin Rohloff, Björn Anke, Siyuan Zhang, Ulrich Gernert, Christina Scheu, Martin Lerch and Anna Fischer, Mo-doped $BiVO_4$ thin films–high photoelectrochemical water splitting performance achieved by a tailored structure and morphology. *Sustainable Energy Fuels*, **2017**,1, 1830-1846

Acknowledgements

This research was supported by *Clean Production System Technology Manufacturing Innovation Research and Development* R&D Program (Pj. No. EH240007) of KITECH funded by MOEF, Republic of Korea.

Core-Shell Chabazite Catalysts for the Tandem Catalysis of CO2 to Light Hydrocarbons:

Renzo A. Leeflang*[1], Volkan Degirmenci[2], Edman S.C. Tsang[1],
[1]*Wolfson Catalysis Centre, Department of Chemistry, University of Oxford, Oxford OX1 3QR, United Kingdom*
[2] *School of Engineering, University of Warwick, Coventry, CV4 7AL, United Kingdom.*
**renzo.leeflang@chem.ox.ac.uk*

Introduction

In recent years increasingly more interest and research has been dedicated to the idea of "the circular carbon economy".[1] Devising catalytic processes, which can serve as alternatives to fossil fuels and their derivatives, is central to such an sustainable economy. As such, there is a need for the development of catalysts capable of converting carbon dioxide to specific products. CO_2 hydrogenation to light hydrocarbons has received much attention. Although substantial progress has been made in CO_2 hydrogenation catalysis to hydrocarbons, controlling the carbon chain length and type (paraffin, olefin, aromatic) remains largely elusive.

To achieve this control zeolites are used. Generally a metal(oxide) catalyst hydrogenates CO_2 to form some intermediate, which is then converted to the desired product by a zeolite catalyst. There are two routes: using a Fisher Tropsch or methanol synthesis (MS) catalyst .

The interplay between the two catalysts is crucial. Coupling two reactions can overcome the thermodynamic limits of the individual reactions [4]. In fact, the "proximity" of the two catalysts can have a large impact on catalytic behaviour. Both conversion and product selectivity can be influenced depending on the nature of the hydrogenation catalyst [5, 6]. In principle, a short distance between the two catalysts is favourable: A short diffusion path between two catalysts should increase pulling effect. However, a minimal distance is required to maintain bi-functionality of the two catalysts with In-based catalysts. In contrast, for Zr-based catalysts "the closer the better" applies.

The difference between In and Zr lies in their reducibility: while Zr is stable within its oxide lattice,[3] In is easily reduced. Hence, In can migrate to the zeolite, causing in-situ ion exchange. This reduces the zeolite acidity, leading to deactivation. As a result, C1 instead of C2+ products are formed. Importantly, the BAS sites on the zeolite facilitate this metal migration. Pacification of the surface can prevent metal migration. Protecting the zeolite from poisoning remains one of the most important challenges to achieve highly active and selective tandem CO_2 hydrogenation catalysis.

We combine a RhIn/MgO catalyst with SSZ-13, which is protected by an all silica shell (SSZ-13@Si-CHA) to inhibit poisoning. To the best of our knowledge, our research is the first to illustrate the effectiveness of SSZ-13@Si-CHA in tandem CO_2 hydrogenation.

Materials and Methods

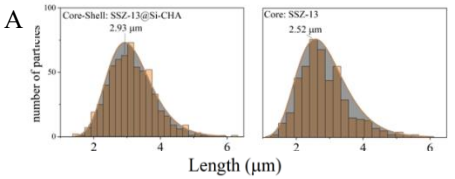
The SSZ-13@Si-CHA is synthesised by a hydrothermal secondary growth procedure according to the methods developed by Miyamoto et al.[3] Our RhIn/MgO catalyst was synthesized by coprecipitation using metal nitrates at a constant pH (~10) using NaOH to form an LDH precursor. The LDH is subsequently exfoliated, calcined and mixed with our SSZ-13@Si-CHA by grinding.

After reduction in 5%H_2 the CO_2 hydrogenation reaction was performed in a fixed-bed flow reactor at 45 bar at 320-380°C. Reaction products and conversion were quantified by GC by internal standard method.

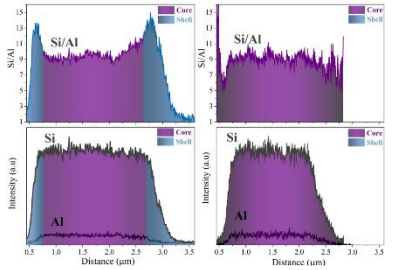
Results and Discussion

The successful formation of the all silica CHA shell has been extensively studied using XPS, XRF, BET, pyridine and NH_3 IR adsorption experiments as well as SEM-EDX (see A &B).

A



B



Importantly, our results clearly show the benefit of surface pacification of SSZ-13. This is evidenced by the substantial suppression of the formation of CO under CO_2 hydrogenation conditions by the presence of the Si-CHA shell compared to the core alone. While the CO selectivity exceeds 60 % using the core SSZ-13, this can be significantly reduced to 20-30% when using a protected zeolite. The remainder of the products consist of light hydrocarbons up to C_4 including a small amount of methane (<10%).

Significance

The catalytic conversion of CO_2 to specific products is essential to establishing a circular carbon economy. To be able to establish such economy catalyst with a high degree of selectivity towards desired products are required. Considering the current challenges of tandem CO_2 conversion, new zeolite catalysts need to be investigated to insure the dual functionality of the catalytic system.

In order to achieve this we have, for the first time, employed RhIn/MgO with combined with a core-shell chabazite zeolite catalyst to prevent in-situ poisoning and control the hydrocarbon product to light hydrocarbons.

References

1. L. M., Alsarhan, A. S. Alayyar, N. B Alqahtani, N. H Khdary, *MPDI*. **2021**. *13(21),* 11625
2. Wang, Y.; Wang, G.; van der Wal, L. I.; Cheng, K.; Zhang, Q.; de Jong, K. P.; Wang, Y. *Angew Chem Int Ed Engl* **2021**, *60* (32), 17735-17743. DOI: 10.1002/anie.202107264 From NLM PubMed-not-MEDLINEX. Wang, P. J. Ramírez, W. Liao, J. A. Rodriguez, P. Liu, *J. Am. Chem. Soc.* **2021**, *143* (33), 13103–13112.
3. Miyamoto, M.; Iwatsuka, H.; Oumi, Y.; Uemiya, S.; Van den Perre, S.; Baron, G. V.; Denayer, J. F. M. *Chemical Engineering Journal* **2019**, *363*, 292-299. DOI: 10.1016/j.cej.2019.01.106.S. Li, H. Guo, C. Luo, H. Zhang, L. Xiong, X. Chen, L. Ma*, Catal. Lett.*, **2013**, 143, 345–355

Selective catalytic cracking of plastic waste for naphtha-like pyrolysis oil production

Petros SOLDATOS[1], Angeliki LEMONIDOU[2], Konstantinos TRIANTAFYLLIDIS[1, *]
[1]*Aristotle University of Thessaloniki, Department of Chemistry, Thessaloniki, Greece.*
[2]*Aristotle University of Thessaloniki, Department of Chemical Engineering, Thessaloniki, Greece.*
** e-mail: ktrianta@chem.auth.gr*

Significance and Relevance

This study examines the in-situ catalytic upgrading of plastic waste pyrolysis oil into naphtha-range hydrocarbons, highlighting the impact of catalyst properties such as acidity and porosity on product composition and distribution. Through the systematic investigation of aluminosilicate catalysts, the work identifies critical factors driving the selective production of C_5–C_{12} hydrocarbons, suitable for direct use (or after mild hydrotreatment) in existing steam cracking units. The findings provide valuable mechanistic insights to guide the subsequent design of advanced catalytic systems for efficient plastic waste valorization, facilitating the conversion to fossil-based raw material and effectively closing the plastics lifecycle loop.

Preferred topic: 1st Circular economy, 2nd Sustainable and clean energy production and transport
Preferred presentation: Poster preferred or short oral

Introduction and Motivations

Plastic waste constitutes nearly 13% of global solid waste, with over 70% either landfilled or incinerated, leading to the the loss of its hydrocarbon-rich polymeric structure. While mechanical recycling is a promising approach, it is often hindered by the heterogeneous and complex nature of real mixed plastic waste streams [1,2]. In contrast, chemical recycling, particularly pyrolysis, offers an alternative by converting plastics into crude py-oils. A critical challenge, however, is upgrading these oils into refined, high-value fractions, like naphtha, capable of reintegration into the plastic production chain [1-3]. The present study addresses this challenge by examining the in-situ catalytic upgrading using aluminosilicate materials to enhance the yield, quality, and selectivity of the resulting py-oils.

Materials and Methods

A fixed-bed reactor was employed under fast pyrolysis conditions (450-700 °C, contact time <1s, N_2 flow: 100 ml/min, plastic/catalyst mass ratio of 10:1) for both thermal and catalytic pyrolysis of LDPE, the major component of real plastic waste streams. The resulting py-oils were analyzed using GC-MS/FID, while gaseous products were collected and analyzed offline via GC-TCD/FID. A broad range of aluminosilicate materials with varying pore sizes, structures, and Si/Al ratios was tested, resulting in differing acidic properties, including variations in the abundance and strength of Brønsted and Lewis acid sites. Catalysts included highly Brønsted acidic microporous crystalline zeolites, like ZSM-5, alongside other zeolitic materials (MOR, FER, Beta, USY, etc.) and mildly acidic mesoporous mixed oxides, such as silica-alumina, which primarily exhibits Lewis acidity, thereby covering a wide range of catalytic properties. Additionally, natural zeolites were evaluated as cost-effective and potentially competitive alternatives. Fresh and spent catalysts were extensively characterized using XRD, FTIR-pyr, N_2 sorption, TGA, elemental analysis, and other complementary techniques.

Results and Discussion

Thermal pyrolysis of LDPE primarily produced heavy waxes (>70 wt%), predominantly consisting of C_{20+} hydrocarbons at temperatures up to 600 °C, with minimal formation of gaseous products and py-oil (both <5 wt%). The introduction of catalysts notably reduced waxes fraction while significantly enhancing both py-oil and gaseous products yields.

Notably, the strongly acidic ZSM-5 (SAR=11.5) demonstrated exceptional catalytic cracking performance, with its small tubular micropores facilitating extensive overcracking. This resulted in over

70 wt% gaseous products at 450 °C, with propylene accounting for up to 20 wt%, underscoring ZSM-5's potential for low-temperature monomer recovery applications. In contrast, zeolites such as Beta, FER, and MOR, despite having similar SAR values, exhibited moderate cracking activity, limiting overcracking and achieving higher py-oil yields of up to 50 wt%. While all catalysts effectively converted heavy waxes into lighter fractions, the balance between wax conversion towards py-oil or gases was strongly influenced by the specific physicochemical properties of each catalyst.

The py-oils produced predominantly fell within the naphtha range, yielding substantial amounts of C_5–C_{12} hydrocarbons (Figure 1). Catalyst acidity was a key determinant in directing the cracking and reforming pathways of pyrolysis vapors. Variations in acid site type and abundance significantly affected product distribution, with Brønsted acidic catalysts favoring paraffin formation and Lewis acid sites promoting olefin production. The aromatic content of py-oils remained consistently low (<10 wt%), a desirable property for steam cracking applications, as aromatics are prone to coke formation. The olefin to paraffin ratio was notably high, with iso-olefins in the C_5-C_7 range dominating the composition. While the high olefinic content makes these oils unsuitable for direct steam cracking, they can be effectively hydrotreated under mild conditions to produce a highly saturated naphtha feedstock. This downstream hydrotreatment step provides a more efficient pathway to high-quality naphtha production, minimizing the need for severe hydrocracking of crude py-oils and enhancing the overall efficiency of plastic waste conversion into valuable hydrocarbons.

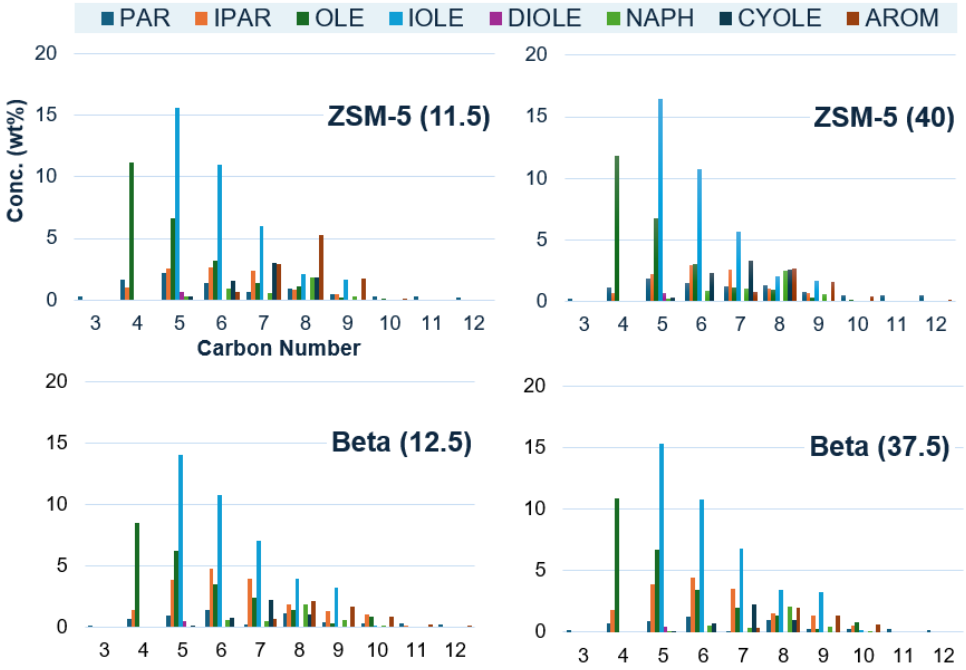


Figure 1 Detailed hydrocarbon analysis of py-oils obtained from different zeolites.

References

1. K. Ragaert, L. Delva, K.V. Geem, *Waste Management* **2017**, *69*, 24-58.
2. K. Hu, Y. Yang, Y. Wang, X. Duan, S. Wang, *Chem Catalysis* **2022,** 4, 724-761.
3. B. Weckhuysen, *Science* **2020**, 6515, 400-401.

Acknowledgements

This research has received funding from the European Union's Horizon Europe research and innovation programme under the HORIZON-CL4-2021-TWIN-TRANSITION-01 grant agreement No 101058412. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or HADEA. Neither the European Union nor the granting authority can be held responsible for them.

Green NH_3 production from NO_x stationary emissions

Giuseppe NAVA[1], Alessandro PORTA[1]*, Roberto MATARRESE[1], Luca LIETTI[1]
[1]*Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano – Via La Masa 34, 20156 Milan, Italy*
** alessandro1.porta@polimi.it*

Significance and Relevance

In this work we demonstrate the possibility to abate NO_x from stationary combustion processes while producing (*green*) NH_3 with high selectivity from renewable H_2 using a cyclic process of capture and conversion at atmospheric pressure. With the right catalyst formulation and the right experimental conditions – compatible with those of combustion flue gases – it is possible to obtain good NH_3 yields while efficiently abating NO_x.

Preferred Topic: Automotive and Stationary Emission Control
Preferred presentation: Oral preferred

Introduction and Motivations

Green ammonia is expected to play a crucial role in the energy transition as it serves as a sustainable base chemical and a versatile energy carrier. With its potential to store and transport hydrogen, it will facilitate the integration of renewable energy sources into various sectors, thus accelerating the shift towards a cleaner and more resilient energy infrastructure[1]. Nowadays, ammonia production is energy intensive, as the energy required to sever the N-N bond is significant. NO_x is a waste toxic compound present in combustion flue gases, which is nowadays abated using NH_3 as a reactant according to the well-established SCR process to comply with environmental regulations. In this scenario, the production of green ammonia using NO_x as N source is very appealing[2], as it could turn emission abatement from a cost to a potential resource, allowing for a decentralized production of green NH_3. Noble metal-based catalysts are established materials in NO_x capture and reduction, and could be well suited to this application. Indeed, typical Lean NOx Traps (LNT) catalysts such as $Pt/Ba/Al_2O_3$ can adsorb NO_x from flue gases and converting it to N_2. Both the adsorption and the reduction of NOx are activated processes: catalytic oxidation of NO is needed to adsorb NO as nitrate/nitrite and catalytic reduction of stored species. The reduction follows a two-step mechanism[3], where stored NO_x is reduced first to NH_3, which then reduces downstream NOx to N_2. Hence, in this work we prepare and test different catalysts and experimental conditions to verify the possibility to efficiently capture NO_x while selectively producing NH_3 upon H_2 exposure.

Materials and Methods

1% Pt, 0.5% Rh or 0.5% Ru are impregnated in equimolar amounts on γ-Al_2O_3 (Sasol Puralox) and calcined at 500 °C; the obtained catalyst is then impregnated with Ba acetate to obtain a nominal Ba loading of 16% and calcined again at 500 °C. The obtained catalysts are then characterized by N_2 physisorption, XRD, SEM-EDS and H_2 chemisorption, and with NO-TPA (Temperature Programmed Adsorption) followed by TPD or H_2-TPSR. Testing is performed in transient conditions cycling an oxidizing adsorption atmosphere (500 ppm NO + 3% O_2, 5 min) with a reducing H_2 pulse (4% H_2, 5 min), spaced out by an inert purge. The system is cycled isothermally in the range 250-350°C. The same experimental conditions are repeated also in the presence of 1% CO_2 and/or H_2O during the adsorption step. Dedicated experiments were replicated using an *operando* FT-IR setup.

Results and Discussion

Cyclic experiments at different temperatures with only NO and O_2 during the adsorption step (**Fig 1A-C**) show the highest NH_3 productivity per cycle on Rh-based catalyst, because of its high NH_3 selectivity and relatively high NO_x uptake. Pt- and Ru-based catalysts lead to lower NH_3 yields, due to low NH_3 selectivity and low NO_x uptake, respectively. These data point out that a trade-off between NO_x storage capacity (favored at higher temperatures) and NH_3 selectivity (favored at lower T) has to be chosen to maximize NH_3 production.

When CO_2 is also present in the adsorption atmosphere, it competes with NO_x for the same adsorption sites and hinders NO_x uptake below 350°C for Rh and Ru-based catalyst, while no significant effects are seen on Pt (**Fig 2A**), suggesting a kinetic inhibition in the case of Rh and Ru in the presence of CO_2. In terms of NH_3 selectivity, in the presence of CO_2 Rh and Ru show minor enhancements while Pt almost doubles its NH_3 selectivity at low temperatures. Accordingly, in terms of NH_3 production (**Fig. 2C**), a substantial decrease is observed for the Rh-based catalyst, no significant changes are visible for the Ru-based catalyst whereas a significant increase in the NH_3 production per cycle at low temperatures is observed for Pt-based catalyst.

Cyclic experiments were replicated in an *operando* FTIR set-up to qualify surface species during adsorption and regeneration cycles. Spectral data indicated that at low temperatures in the presence of CO_2 and NO_x, nitrates/nitrites and carbonates coexist on the catalyst surface, while at high temperatures nitrates dominate by far the pool of adsorbed species. At low temperatures, when the atmosphere is switched to reducing conditions, stored carbonates are reduced to CO: this adsorbs on the noble metal, creating a poisoning effect and reducing the catalytically active sites that are able to convert NH_3 and stored NO_x to N_2, thus increasing the NH_3 selectivity.

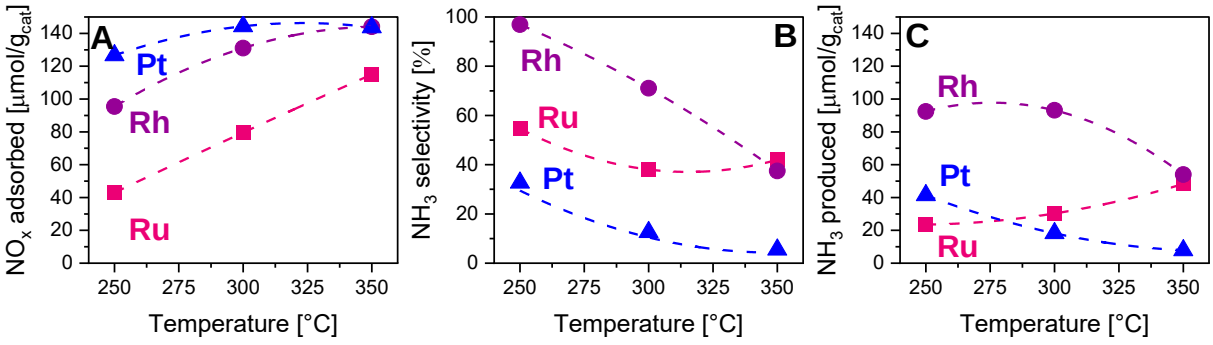


Figure 1. NO_x uptake (A), NH_3 selectivity (B) and NH_3 production (C) per isothermal cycle. Process conditions = Adsorption: 500 ppm NO + 3% O_2/He, 5 min; Reduction: 4% H_2/He, 5 min; constant GHSV = 100 L(STP)/h/g

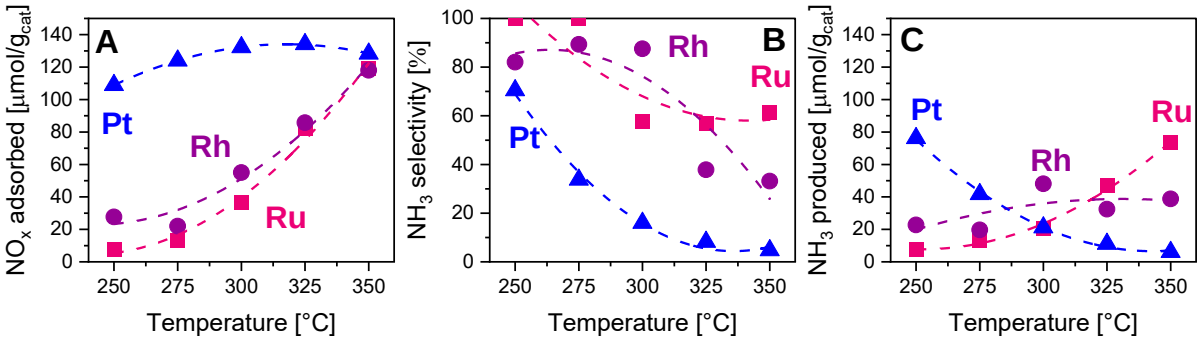


Figure 2. NO_x uptake (A), NH_3 selectivity (B) and NH_3 production (C) per isothermal cycle. Process conditions = Adsorption: 500 ppm NO + 1% CO_2 + 3% O_2/He, 5 min; Reduction: 4% H_2/He, 5 min; constant GHSV = 100 L(STP)/h/g

References

1. Macfarlane et al., Joule 4 (6), 2020, 1186-1205
2. Kobayashi et al., Catal Sci Technol 13, 2023, 297-300
3. Cumaranatunge et al., J Catal 246, 2007, 29-34

Ionic Liquid-Assisted Synthesis of Fe-Ru Bimetallic Catalysts for Enhanced CO_2 Conversion to Lower Olefins with High Selectivity

Marina MADDALONI[1], Ander CENTENO-PEDRAZO[2], Simone AVANZI[1], Nayan Jyoti MAZUMDAR[2], Haresh MANYAR[2] and Nancy ARTIOLI[1]*

[1]CEEP Laboratory, Department of Civil Engineering, Architecture, Territory, Environment and Mathematics, University of Brescia, via Branze 38, 25123 Brescia, Italy;

[2]School of Chemistry and Chemical Engineering, Queen's University Belfast, David-Keir Building, Stranmillis Road, Belfast, BT9 5AG, UK

*nancy.artioli@unibs.it

Significance and Relevance

This study demonstrates the enhanced synergy between Fe and Ru nanoparticles (NPs) in Fe-Ru bimetallic catalysts synthesized using an ionic liquid (IL) method, which outperforms traditional colloidal synthesis in producing short-chain hydrocarbons. This innovative synthesis approach improves CO_2 conversion efficiency, creating pathways for sustainable applications such as the production of carbon-neutral e-fuels and the use of CO_2 as a renewable carbon source.

Preferred and 2nd choice for the topic:
1st choice: Sustainable and clean energy production and transport;
2nd choice: CO_2 utilization and recycling.
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The direct conversion of carbon dioxide into lower olefins (C_2-C_4) offers a promising sustainable production pathway[1,2]. These lower olefins—ethylene, propylene, and butene—are essential in the chemical industry and for the production of Liquefied Petroleum Gas (LPG). This reaction involves two main steps: the Reverse Water Gas Shift (RWGS) reaction, which produces CO, followed by CO's conversion to hydrocarbons through the Fischer–Tropsch reaction[3]. Recent research has demonstrated the cost-effectiveness and effectiveness of Fe-based catalysts in these stages, especially in combination with Ru to enhance olefin selectivity[4,5].

In this study, an innovative synthesis approach leverages ionic liquids as reaction media, providing precise control over Fe and Ru nanoparticle sizes and ensuring an even distribution of active metal phases. This ionic liquid method improves upon traditional colloidal techniques, yielding a significantly higher selectivity for target hydrocarbons, highlighting the potential of ionic liquids in advancing catalyst design for CO_2 conversion.

Materials and Methods

In the ionic liquid (IL)-assisted method, [BmIm][BF_4] was combined with either $Fe(acac)_3$ or $Ru_3(CO)_{12}$ to synthesize nanoparticles (NPs) at 523 K over 18 hours. For bimetallic Fe-Ru NPs, three different molar ratios (1:1, 3:1, and 9:1) were explored, and the resulting nanocatalysts were supported on γ-Al_2O_3 with metal loadings of either 1 wt.% or 4 wt.%. The catalysts were characterized using XRF, XRD, SEM, and H_2 chemisorption. Kinetic experiments were conducted at 593 K and 20 bar.

Results and Discussion

Fe_2O_3-RuO_2/Al_2O_3 catalysts synthesized using ionic liquid (IL) methods were analyzed through SEM and XRF to confirm the homogeneous distribution of nanoparticles (NPs) on the Al_2O_3 support and verify the targeted Fe/Ru ratio (**Figure 1**).

The redox properties of catalysts prepared by both traditional colloidal (COL) and IL methods were investigated via TPR (**Figure 2a**) for Fe and Fe/Ru catalysts. Both catalyst sets exhibited two distinct

reduction steps: Fe_2O_3 to Fe_3O_4 (620 K), Fe_3O_4 to FeO (800 K), and further reduction to FeO and Fe^0 (900 K). The inclusion of RuO_2 lowered the reduction temperature, indicating enhanced reduction of Fe species and hydrogen spillover from Ru to Fe_2O_3. The IL method revealed distinct behavior, with no noticeable peak corresponding to the reduction of Ru^{4+} to Ru^0 (380 K). When varying the Fe/Ru ratio in the IL catalysts, it was observed that the reduction peak is shifted at lower temperature (XX) as Ru reduction occurred first, highlighting improved reducibility through increased cooperation between Fe and Ru species due to their closer proximity.

These variations in reducibility were consistent with changes in catalytic performance at 20 bars (**Figure 2b**). Notably, the IL-synthesized catalysts achieved a five-fold increase in CO_2 conversion compared to the colloidal one. Additionally, increasing the metal loading from 1 wt% to 4 wt% significantly enhanced selectivity for CH_4 and C_2-C_5 hydrocarbons.

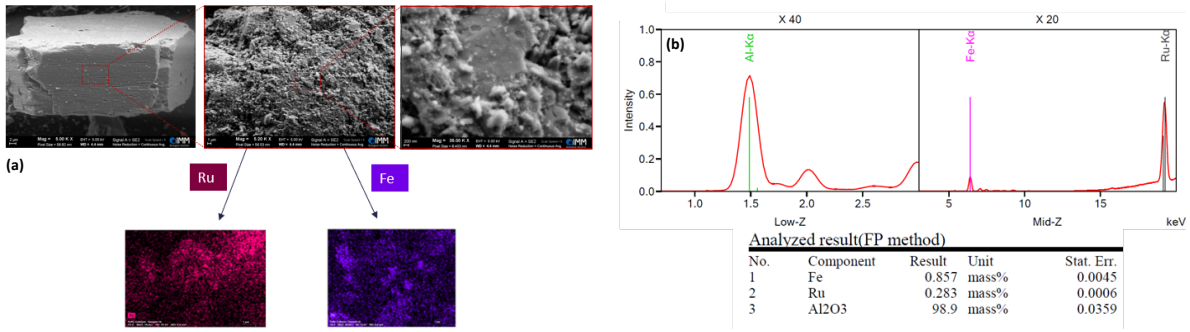


Figure 1. a) SEM-EDX analysis of the 1wt% Fe-Ru 3:1/Al_2O_3 (IL) sample. **b)** XRF analysis of the 1wt% Fe-Ru 3:1/Al_2O_3 (IL) sample.

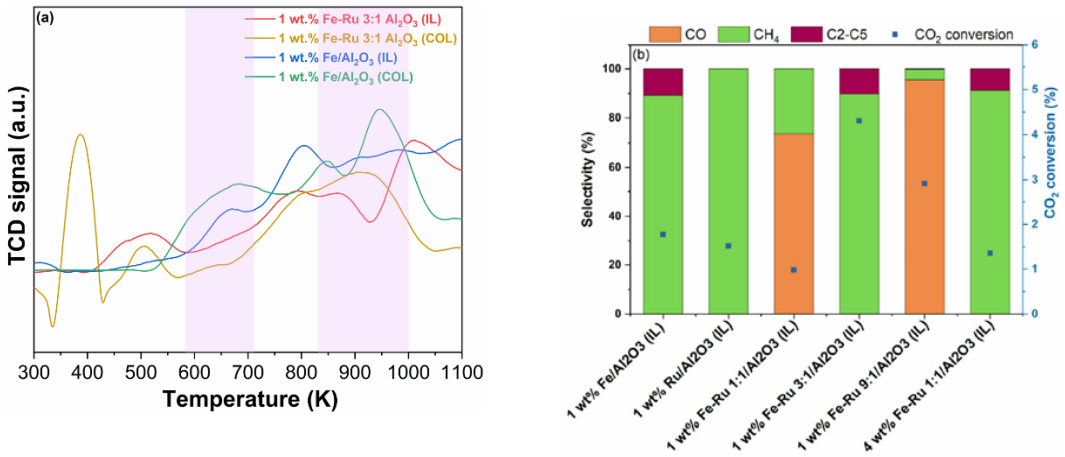


Figure 2. a) Comparison of the TPR profiles of the 1wt% Fe-Ru 3:1/Al_2O_3 IL and COL catalysts. **b)** CO_2 conversion (%) and selectivity for IL catalysts at 20 bar and 45 mL/min.

References

1. IPCC, Global warming of 1.5°C, 2022.
2. H. Yang, C. Zhang, P. Gao, H. Wang, X. Li, L. Zhong, W. Wei and Y. Sun, Catal. Sci. Technol., 2017, 7, 4580–4598.
3. M. D. Porosoff, B. Yan and J. G. Chen, Energy Environ. Sci., 2016, 9, 62–73.
4. R. W. Dorner, D. R. Hardy, F. W. Williams and H. D. Willauer, Energy Environ. Sci., 2010, 3, 884–890.
5. T. Riedel, M. Claeys, H. Schulz, G. Schaub, S. S. Nam, K. W. Jun, M. J. Choi, G. Kishan and K. W. Lee, Appl. Catal. A Gen., 1999, 186, 201–213.

Solid Catalyst with Ionic Liquid Layer (SCILL) for Direct CO_2 Hydrogenation to Methanol: Enhancing Performance and Stability

Giuseppe BAGNATO[1], Emilia MORROW[1], Hannah AGNEW[1], Małgorzata SWADŹBA-KWAŚNY[1] and Nancy ARTIOLI[2] *

[1]School of Chemistry and Chemical Engineering, Queen's University Belfast, David-Keir Building, Stranmillis Road, Belfast, BT9 5AG, UK

[2]CEEP Laboratory, Department of Civil Engineering, Architecture, Territory, Environment and Mathematics, University of Brescia, via Branze 38, 25123 Brescia, Italy;

*nancy.artioli@unibs.it

Significance and Relevance

This research investigates the use of **S**olid **C**atalysts with **I**onic **L**iquid Layers (**SCILL**) for CO_2 direct hydrogenation to methanol with copper-based methanol synthesis catalysts (CZA). Ionic liquids (ILs), known as "designer solvents" for their tunable properties, offer excellent gas solubility, particularly for CO2, making them ideal for enhancing catalytic processes like hydrogenation and enabling efficient, high-temperature applications. Initial results indicated lower methanol yields compared to the uncoated heterogeneous catalyst, likely due to stability issues with the **SCILL** system in the presence of water. However, the introduction of Ionic liquid Li[NTf_2] doping led to a significant improvement in catalytic performance, enhancing CH_3OH conversion rates compared to traditional CZA. Additionally, this doping increased system stability, especially in the presence of water. These results highlight the potential of SCILL catalysts as a more efficient and stable solution for CO_2 hydrogenation, contributing to sustainable methanol production and CO_2 mitigation.

Preferred and 2nd choice for the topic:
1st choice: CO_2 utilization and recycling;
2nd choice: Sustainable and clean energy production and transport.
Preferred presentation: *Poster*

Introduction and Motivations

This study explores an innovative method for CO_2 hydrogenation to methanol, aiming to enhance conversion efficiency through a Solid Catalyst with Ionic Liquid Layer (SCILL). By integrating an ionic liquid (IL) layer onto a commercial Cu/ZnO/Al_2O_3 catalyst, we aim to improve both stability and catalytic performance. Initially, various ILs were evaluated for their thermal stability using advanced thermogravimetric analysis (TGA). The most stable ILs were selected to form SCILL catalysts with a 10% IL loading. When tested for CO_2 hydrogenation, the SCILL catalysts exhibited significantly improved CO_2 conversion rates compared to conventional catalysts. Furthermore, the incorporation of Li[NTf_2] into the SCILL system enhanced its stability, mitigating the adverse effects of water deactivation observed in untreated SCILL catalysts.

Materials and Methods

In this work, several ionic liquids (ILs), including [PPh_4][$C_4F_9SO_3$], [SPh_3][$C_8F_{17}SO_3$], [SPh_3][$C_4F_9SO_3$], [PPh_4][NTf_2], and [SPh_3][NTf_2], were explored alongside a copper-based catalyst (CZA) to develop Solid Catalysts with Ionic Liquid Layers (SCILL). The SCILL catalysts were prepared by combining CZA with ILs in methanol, while doping with Li[NTf2] further modified the system. A thorough characterization of the materials was conducted using techniques such as ICP-OES, BET surface area analysis, XRD, and TPR. The stability of the ILs was studied through dynamic and isothermal TGA, and their degradation behavior was analyzed. The study also assessed the performance and longevity of these ILs under reaction conditions rich in hydrogen. Finally, reactor tests for CO_2 hydrogenation were carried out at 250°C and 20 bar (CO_2/H_2 ratio of 1:3) to evaluate both the SCILL catalysts and the commercial CZA catalyst, providing insights into their practical applications and stability.

Results and Discussion

This study investigates the hydrogenation of CO_2 using a commercial copper-zinc-alumina (CZA) catalyst and a Solid Catalyst with Ionic Liquid Layer (SCILL) system. A range of ionic liquids (ILs), including $[PPh_4][C_4F_9SO_3]$, $[SPh_3][C_8F_{17}SO_3]$, $[PPh_4][NTf_2]$, and others, were synthesized and characterized to assess their thermal stability for SCILL applications. Two ILs, $[PPh_4][C_4F_9SO_3]$ and $[PPh_4][NTf_2]$, were identified as the most thermally stable, with $[PPh_4][NTf_2]$ showing the highest activation energy (Ea) and pre-exponential factor, suggesting excellent thermal stability under reaction conditions.

Table 1. *Results from Arrhenius plots and errors calculated through validation of the kinetic model*

IL	Activation Energy [kJ/mol]	Pre-exponential factor [h^{-1}]	R^2	Validation T [°C]	Mass error after 10 h [%]
$[PPh_4][C_4F_9SO_3]$	139.9	$2.38 \cdot 10^{12}$	0.9903	273	0.64
$[PPh_4][NTf_2]$	182.2	$4.98 \cdot 10^{15}$	0.9922	295	0.04

These ILs were subjected to thermal stability tests in nitrogen at 250°C and 20 bar over 10 hours, where they showed good resistance. However, degradation was observed in a $CO_2/H_2/H_2O$ mixture. To enhance the system's stability, SCILLs were doped with $Li[NTf_2]$, which significantly improved stability, allowing the doped systems to retain CO_2 absorption capabilities under harsh reaction conditions.

The performance of these doped SCILL systems was evaluated in CO2 hydrogenation reactions (250°C, 20 bar, CO_2/H_2 1:3) over 35 hours. $[PPh_4][C_4F_9SO_3]$ doped with $Li[NTf_2]$ achieved a 25% CO_2 conversion rate, outperforming both the commercial CZA catalyst (10%) and the undoped $[PPh_4][NTf_2]$ (2%). However, the doped system showed a shift in selectivity, favoring CO production instead of methanol. NMR analysis revealed degradation of the phenyl group in $[PPh_4][NTf_2]$, contributing to changes in the product distribution. These results demonstrate the potential of SCILL systems to enhance CO_2 hydrogenation efficiency while highlighting the trade-off in selectivity.

Table 2. *Results of catalytic testing at 250°C and 20 bar, CO2/H2 1:3*

	X CO_2 (%)	Selectivity (%)				
		CH_4	Acetone	DME	CH_3OH	CO
CZA	10.0	0	1.61	8.86	21.9	67.62
$[PPh_4][C_4F_9SO_3]$ doped $Li[NTf_2]$	25.0	0	0	0.15	0.03	99.83
$[PPh_4][NTf_2]$ doped $Li[NTf_2]$	3.4	0.05	0	1	2.88	96.06

References

1. P. Gabrielli, M. Gazzani and M. Mazzotti, Ind. Eng. Chem. Res., 2020, 59, 7033–7045
2. M. Scheuermeyer, M. Kusche, F. Agel, P. Schreiber, F. Maier, H. P. Steinrück, J. H. Davis, F. Heym, A. Jess and P. Wasserscheid, New J. Chem., 2016, 40, 7157–7161
3. J. Reichert, S. Maerten, K. Meltzer, A. Tremel, M. Baldauf, P. Wasserscheid and J. Albert, Sustain. Energy Fuels, 2019, 3, 3399–3405.

Cu-Ce binary oxide catalysts for CO_2 hydrogenation to methanol: Operando FT-IR spectroscopy and kinetic study

Marco Pietro MEZZAPESA*[,1], Fabio SALOMONE[1], Enrico SARTORETTI[1], Raffale PIRONE[1], Samir BENSAID[1]
[1]*Politecnico di Torino, Department of Applied Science and Technology (DISAT), Corso Duca degli Abruzzi 24, 10129 Turin, Italy.*
** marco.mezzapesa@polito.it*

Significance and Relevance

This research is significant for advancing sustainable chemical processes by improving CO_2 hydrogenation to methanol, a key industrial chemical. This study of Cu-CeO_2 catalysts highlights the importance of the Cu/Ce ratio and the synthesis technique in optimizing methanol yield. Investigating the relationship between catalyst morphology (e.g., copper particle size) and performance, alongside *in-situ* and *operando* analyses to understand reaction mechanisms and material properties, offers crucial insights for the design of more efficient catalysts.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling / Fundamental advances in understanding catalysis
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

In the pursuit of a more sustainable and environmentally responsible future, the conversion of CO_2 into valuable chemicals and fuels has emerged as a crucial research frontier. Among the CO_2 hydrogenation reactions, its conversion to methanol appears as a key process in sustainable chemistry, due to the possible use of this substance as a fuel additive, chemical feedstock, for energy storage, etc. Currently, the hydrogenation of CO_2 to methanol is industrially performed using a Cu-ZnO-Al_2O_3 catalyst[1]. This industrial catalyst shows good CO_2 conversion, but the methanol selectivity is not optimal. In this sense, different alternative catalysts have been tested to increase the overall catalytic performance. Among the various possibilities, Cu and CeO_2 show a good synergistic effect for the CO_2 activation in the hydrogenation to methanol process[1,2]. Based on this consideration, the aim of this work is the study of Cu-CeO_2 catalysts and the implementation of *operando* FT-IR techniques to deepen the knowledge of reaction mechanisms.

Materials and Methods

The Cu-Ce binary oxide catalysts were synthesized using three methods—solution combustion synthesis (scs-), wet impregnation (wi-), and gel-oxalate coprecipitation (ox-)—by varying the Cu/Ce atomic ratio (Cu_xCe_{100-x}). Their physicochemical properties were studied with complementary techniques. Catalytic activity and stability were assessed in a steel fixed-bed reactor (25 bar, 200–300 °C, H_2:CO_2:N_2= 3:1:1, 20 NL/h/g_{cat}). After testing, the spent catalysts were further characterized, and static FT-IR spectroscopy in transmittance mode was employed to assess the properties of the materials, such as basicity and their interaction with specific probe molecules. Additionally, the best-performing catalyst was analyzed using *operando* FT-IR spectroscopy in transmittance mode (H_2/CO_2 = 3:1, 5 bar, 200–350 °C) to investigate the reaction mechanism.

Results and Discussion

The catalytic tests identified ox-$Cu_{80}Ce_{20}$ as the best-performing catalyst, achieving a methanol yield of 0.82% at 300 °C. Using this data and applying the Arrhenius equation, the apparent activation energy for CO_2 hydrogenation was estimated. The coprecipitated catalyst (ox-$Cu_{80}Ce_{20}$) exhibited the lowest activation energy (Ea ≈ 80 kJ/mol) and the highest number of active sites, as inferred from the pre-exponential factor (calculated at equal activation energy). Figure 1 summarizes these findings. This high catalytic activity is attributed to the small size of copper particles, which expose more copper surface and enhance the synergistic effect with CeO_2. A detailed spectroscopic analysis was

subsequently carried out on this catalyst. First, the interaction between the ox-CeO_2 support and methanol was investigated using *in-situ* FT-IR spectroscopy. Figure 2(a) shows the region between 775 and 1200 cm^{-1}, where surface methoxy species signals appear as methanol pressure increases. Subsequent heat treatments in vacuum revealed that these species begin to decompose at 250 °C, indicating their relative stability. Additionally, ox-$Cu_{80}Ce_{20}$ was analyzed using *operando* FT-IR spectroscopy. As shown in Figure 2(b), the spectra revealed an intensifying peak in the 800-900 cm^{-1} region with an increasing temperature, indicating the formation of bidentate carbonates above 320 °C due to CO_2 activation. Carbonate species play a specific role in methanol synthesis, inhibiting CO hydrogenation to methanol at the Cu-CeO_2 interface. However, they do not completely inhibit the methanol synthesis reaction, as CO_2 hydrogenation to methanol proceeds on the Cu surface through the formation of formate intermediates. These findings provide valuable insights into the design of more efficient catalysts for CO_2 hydrogenation to methanol.

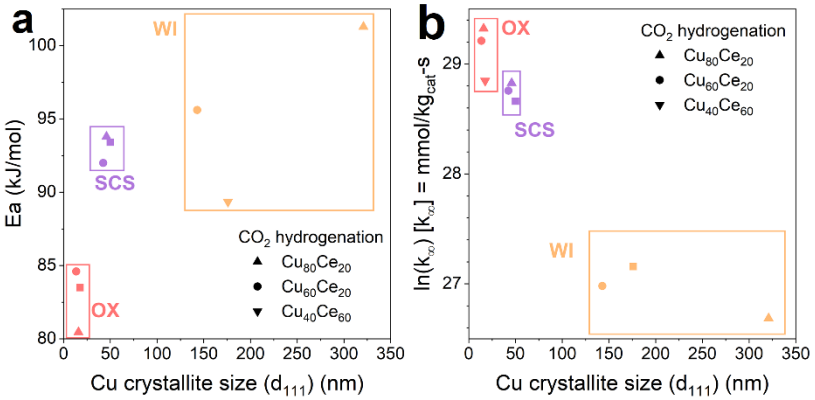


Figure 1. Arrhenius equation parameters as a function of copper particle size (calculated using the Scherrer equation): **(a)** apparent activation energy, Ea, and **(b)** pre-exponential factor (estimated under the assumption of equal activation energy), $ln(k_\infty)$.

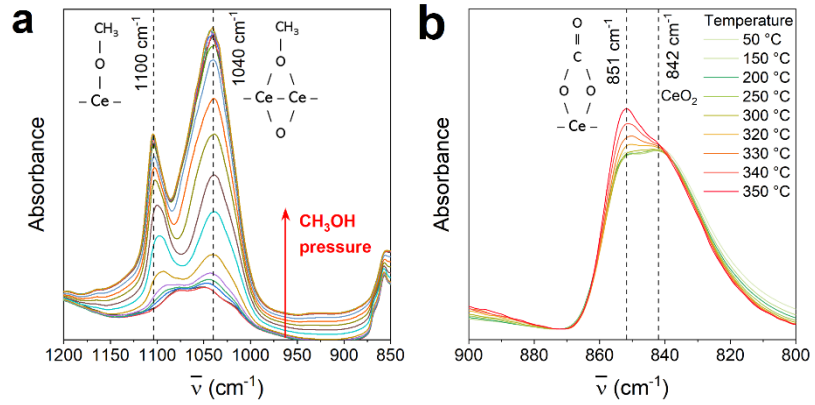


Figure 2. (a) FT-IR spectra obtained for ox-CeO_2 during *in-situ* analyses with methanol as a probe molecule. **(b)** FT-IR spectra obtained for ox-$Cu_{80}Ce_{20}$ during *operando* analysis at 5 bar with a 15 NmL/min flow of H_2:CO_2 = 3:1 mixture.

References

1. A. Álvarez, A. Bansode, A. Urakawa et al., *Chem. Rev.* **2017**, *117*, 9804-9838
2. J. Graciani, K. Mudiyanselage, F. Xu et al., *Science* **2014**, *345*, 546-550
3. E. Sartoretti, C. Novara, M.C. Paganini et al., *Catalysis Today* **2023**, *420*, 114037
4. L. Lin, S. Yao, Z. Liu et al., *J. Phys. Chem. C* **2018**, *122*, 12934-12943

Acknowledgments

Fabio Salomone and Enrico Sartoretti acknowledge the Italian Ministry of University and Research (MUR), program FSE REACT-EU PON Ricerca e Innovazione 2014-2020 (D.M. 1062/2021). Project funded under the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3 - Call for tender No. 1561 of 11.10.2022 of Ministero dell'Università e della Ricerca (MUR); funded by the European Union – NextGenerationEU. Project code PE0000021, Concession Decree No. 1561 of 11.10.2022 adopted by Ministero dell'Università e della Ricerca (MUR), CUP - to be indicated by each Beneficiary, according to attachment E of Decree No. 1561/2022, Project title "Network 4 Energy Sustainable Transition – NEST".

Silica supported DFM catalysts for CO_2 Capture, Storage and Re-use Technology. Comparative study with Al_2O_3-based model catalyst.

Sergio Molina-Ramírez[1], Giuseppe Nava[2], Cinzia Cristiani[1], Barbara Di Credico[3], Roberto Scotti[3], Luca Lietti[2], Lidia Castoldi[2], Elisabetta Finocchio[*,4]

[1]*Dipartimento di Chimica, Materiali e Ingegneria Chimica Giulio Natta, Politecnico di Milano, Milano, Italy.*

[2]*Dipartimento di Energia (Laboratory of Catalysis and Catalytic Processes), Politecnico di Milano, Milano, Italy.*

[3]*Dipartimento di Scienza dei Materiali, Università Milano-Bicocca, Milano, Italy.*

[4]*Dipartimento di Ingegneria Civile, Chimica e Ambientale, Università di Genova, Genova, Italy.*

*elisabetta.finocchio@unige.it

Introduction and Motivations

The growing concern about global warming and climate change has driven many countries to take action and generate new policies for environmental protection. CO_2 is considered the largest source of greenhouse gas (GHG) emissions. Although decarbonization technologies and strategies show a rapid and steadily developing, they are still incipient and require high investments. CO_2 Capture and Storage and Utilization (CCSU) catalytic strategies have emerged to prevent the CO_2 releasing and reduce its atmospheric concentration. In this context, dual-function materials (DFM) are potentially proposed for cyclic CO_2 capture and methanation technology, acting as both as solid adsorbents catalytic materials for carbon capture for capture CO_2 (the material is exposed to a CO_2-containing gas stream until saturation, enabled by the functionalization with alkaline and/or alkaline-earth) and as catalysts for fuel production upon H_2 exposure (where the CO_2^{stored} is converted to CH_4 through catalytic hydrogenation, $CO_2+4H_2 \rightarrow CH_4+2H_2O$, typically improved by the incorporation of metals such as Ru or Ni)[1]. In literature, successful DFMs consist of redox metals-supported mostly over alumina and doped with alkaline or alkaline-earth ions[2]. However, the growing interest in the use of more economical materials within the idea of circular economy has positioned silica as a possible effective alternative as a catalytic support for DFMs due to its interesting morphological, physical and chemical properties and its use as a fundamental material in numerous industrial applications. Moreover, the recovered silica from industrial wastes could be employed and reused as silica-based support[3].

This contribution presents a comparative study of the catalytic performance with the analysis of the surface-species involved in the cyclic alternating catalytic process of CO_2 capture and reuse of DFMs supported on a commercial silica compared to model DFMs supported on alumina.

Materials and Methods

Silica-supported ternary catalysts were prepared by sequential impregnation as previously reported, incorporating Ru (0.5% wt), and different Alkaline(-earth) oxides such as Ba and K (16% wt)[2]. These catalysts, together with the binary formulations (Me/SiO_2) and the support (commercial silica) were characterized by N_2 physisorption, XRD, SEM-EDX, CO_2 TPD, H_2-TPR, among others. Microreactor experiments were carried out in a quartz tubular reactor, with a space velocity of 100 L(STP)/h/g. The gases leaving the reactor were analyzed by means of a mass spectrometer, a FT-IR spectrometer, and a micro gas chromatograph. CO_2 capture/reduction cycles were performed at constant temperature in the range 250-400°C. Every cycle is composed by an adsorption phase (1% CO_2/He) and a reduction phase (4% H_2/He), separated by an inert purge. Advanced spectroscopy characterization methodology was carried out for silica and alumina-based-DFMs to investigate acidity and basicity and surface OH groups distribution. CO_2 adsorption and desorption was also tested using *in situ* FT-IR techniques. A

Results and discussion

The catalytic performance data for CO_2 reduction with H_2 are presented in Table 1. CO_2 conversion achieved by Ru-Ba catalysts appears to be independent of the support material (Al_2O_3 or SiO_2). However, Ru-Ba/SiO_2 shows a higher methane selectivity compared to Ru-Ba/Al_2O_3 with same composition at lower temperature range, achieving comparable values beyond 400°C. The CO_2 storage capacity of Ru-Ba/SiO_2 was approximately 230 µmol/g_{cat} (43% lower than that of the Al_2O_3-supported

catalyst), producing 63 µmol/g_{cat} of CH_4 in the subsequent reduction with H_2. This observation implies that not regenerable carbonate species may remain on the surface after the reduction step which do not take part in the methanation reaction.

Table 1. TPR experiment results: temperature ramp (from RT to 500°C @10°C/min) in CO_2 (1% v/v) + H_2 (4% v/v) He-balanced.

Temperature (ºC)	Ru/SiO_2		$Ru-Ba/SiO_2$		$Ru-Ba/Al_2O_3$	
	$_2$(%)	$_4$(%)	$_2$(%)	$_4$(%)	$_2$(%)	$_4$(%)
300	20.0	95.1	11.7	86.1	4.4	41.1
400	29.5	58.2	33.1	39.2	32.0	16.1
500	52.8	20.3	53.6	12.9	53.2	6.8

Experiments conducted with FTIR analysis of the species arising from CO_2 adsorption (Fig. 1), revealed the formation of a complex population of carbonate-type species over the catalyst surface, also depending on the support material employed. Both samples exhibited an initial population of bulky carbonates related to the presence of Ba (1400–1500 cm^{-1} region) stable up to 500ºC. Adsorbed surface and carbonates (likely bidentate species) are detected on both samples, remaining stable following degassing. Hydrogen carbonate species observed in the Al_2O_3-supported catalyst (1227 cm^{-1}) are likely due to the interaction of CO_2 with the support itself, while the same species could be formed over the silica supported catalysts following interaction of CO_2 with the basic oxide phase. However, in the Ru-Ba/Al_2O_3 sample (Fig. 1b), signals around 1560 and 1355 cm^{-1}—linked to the presence of bidentate carbonates on the Ba phase—shifted in the silica-supported material (Fig. 1a), indicating a different nature of these species, which remained present only in Ru-Ba/Al_2O_3 after degassing. These data might be related to the lower CO_2 capture capacity in comparation with Al_2O_3-supported materials.

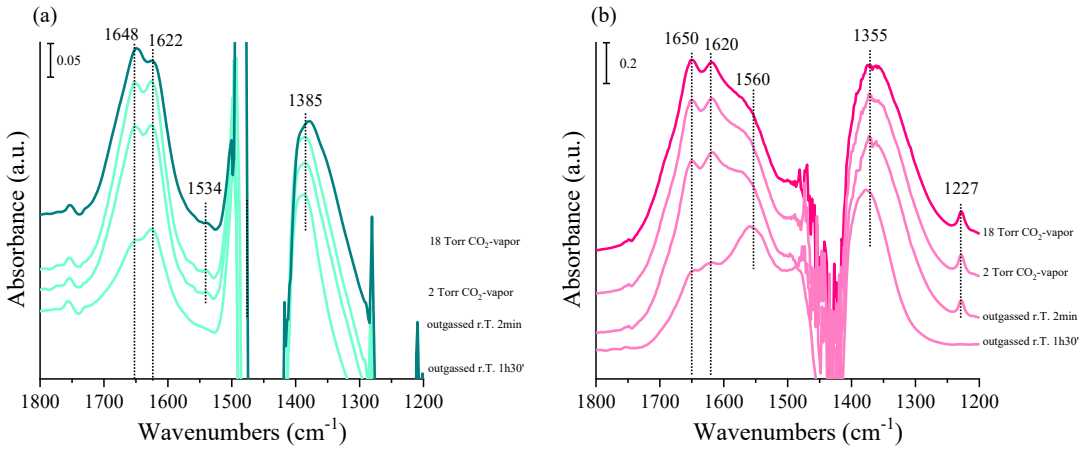


Figure 1. FT IR spectra of surface species arising from CO_2 adsorption and desorption at R.T. for (a) Ru-Ba/SiO_2 and (b) Ru-Ba/Al_2O_3. Activated spectrum was subtracted.

The use of silica as a catalytic support for synthesizing DFMs emerges as a sustainable alternative to Al_2O_3, enabling the development of catalysts with high CO_2 capture capacity, with the capacity of generation of more labile carbonate species, and with a significant catalytic performance in CO_2 Capture and Re-Use process for stationary sources.

References

1. M. Duyar, M. Treviño, R. Farrauto, *Applied Catalysis B* **2015**, 168-169, 370-376.
2. A. Porta, R. Matarrese, C. Visconti, L. Lietti, *Energy&Fuels* **2023**, 37, 7280-7290.
3. M. Vacca, C. Cara, V. Mameli et al., *ACS Sustainable Chem.&Eng.* **2020**, 8, 14286-14300

Acknowledgements

Authors acknowledge financial support of PRIN2022 PNRR SILCO (n. P2022SZANL) Project from the Italian Ministry of University and Research (MUR).

Getting $CuO/ZnO/ZrO_2$ in shape: Tableting of methanol catalysts

Fabian NEUMANN[1], Lucas WARMUTH[1], Thomas N. OTTO[1], Thomas A. ZEVACO[1], Michael ZIMMERMANN[1], Stephan PITTER[1], Moritz WOLF[*,1]

[1]*Karlsruhe Institute of Technology (KIT), Institute of Catalysis Research and Technology (IKFT), Hermann-von-Helmoltz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.*

** moritz.wolf@kit.edu*

Significance and Relevance

In this study a scientific approach towards catalyst shaping by tableting to enable a rational design of shaped catalyst bodies is presented. A moderate content of graphite as a lubricant was shown to be a compromise between a high mechanical stability and a sufficient level of lubrication, facilitating a continuous tableting process. Moreover, a variation of the compaction pressure revealed that the right choice could limit the drawbacks on desirable physico-chemical properties like porosity while keeping a high and even more reliable mechanical stability.

Preferred and 2nd choice for the topic: Preferred: CO_2 utilization and recycling, 2nd choice: Circular Economy

Preferred presentation: Poster

Introduction and Motivations

Shaping of catalysts into bodies, also called technical catalysts, is a major part of catalyst development in order to employ them in industrial reactors. Avoiding high pressure drops in fixed-bed reactors is one of the main reasons that make shaping of powdered catalysts necessary. While the catalytic performance of powdered catalysts is mainly the focus of academia, additional properties, such as mechanical stability and mass transfer, become important during the scale-up into technical catalysts.[1-3] Tableting is a well-established shaping method. Here, the catalyst is compacted between two punches into highly uniform and mechanically resistant bodies.[2,3] In general, catalyst shaping is a topic mainly driven by industrial manufacturers and in part governed by comprehensive empirical knowledge. Although of major importance for the performance and stability of the final catalyst, in-depth understanding of the processes at play and of their influence on the catalytic performance is still lacking in the open literature.[1,2] Therefore, systematic research of the shaping processes is important for a rational design of technical catalysts based on fundamental criteria and can help to bridge existing gaps between catalyst development in academia and industry.

Results and Discussion

Herein, a scientific approach towards catalyst shaping by tableting and its impact on the mechanical and physico-chemical properties is presented. For this purpose, a highly instrumented tableting machine was utilized, which is a powerful device for tablet development as it enables not only fundamental research of the compaction process and the resulting material properties, but also initial scale-up studies.

Tableting was studied for a co-precipitated $CuO/ZnO/ZrO_2$ catalyst for methanol synthesis from CO_2-rich synthesis gas.[4] At first, the effect of different parameters on the tableting process and the mechanical stability of the resulting flat cylindrical tablets was studied: pre-granulation procedure, content of the lubricant graphite, compaction pressure, compaction speed, tablet size as well as an additional pre-compaction step. Based on the results of the initial studies, a detailed investigation of the compaction pressure and the tablet density was enabled by a variation of the tablet weight for well-defined cylindrical mini tablets (2 x 2 mm), which were characterized by a broad range of measurement techniques.

The variation of the content of graphite used as a lubricant revealed a correlation with the ejection force of the tablets as well as the transmission ratio of the pressure from the lower to the upper punch. Lower graphite contents resulted a higher ejection force and a lower transmission ratio of the compaction pressure. Additionally, at the lowest graphite content the production of multiple tablets

was accompanied by a continuous increase of the ejection force and decrease of the transmission ratio. Lubrication is improved at higher graphite contents leading to lower and constant ejection forces and higher transmission ratios. Here, a plateau is reached at moderate levels of graphite. In contrast, measurement of the side crushing strength showed that a higher mechanical stability is favored by lower graphite contents.

Based on these results, further detailed studies of compaction pressure and tablet density were conducted. For the mechanical stability a linear relationship was observed in the lower compaction pressure and tablet density range (Figure 1, left). In the higher range, the increase in crushing strength is less pronounced, less reproducible and accompanied by tablet defects. Porosity was studied by N_2 physisorption and Hg porosimetry to link the changing contributions of micro-, meso- and macropores to the overall porosity with the compaction pressure (Figure 1, right). Tableting was shown to have a negative impact on the reducibility, which was evaluated by temperature-programmed reduction. Increasing compaction pressures led to higher reduction temperatures, a broadening of the reduction peaks and lower hydrogen uptake. Moreover, reduced tablets were smaller in size and showed a change in mechanical resistance, depending on their initial density.

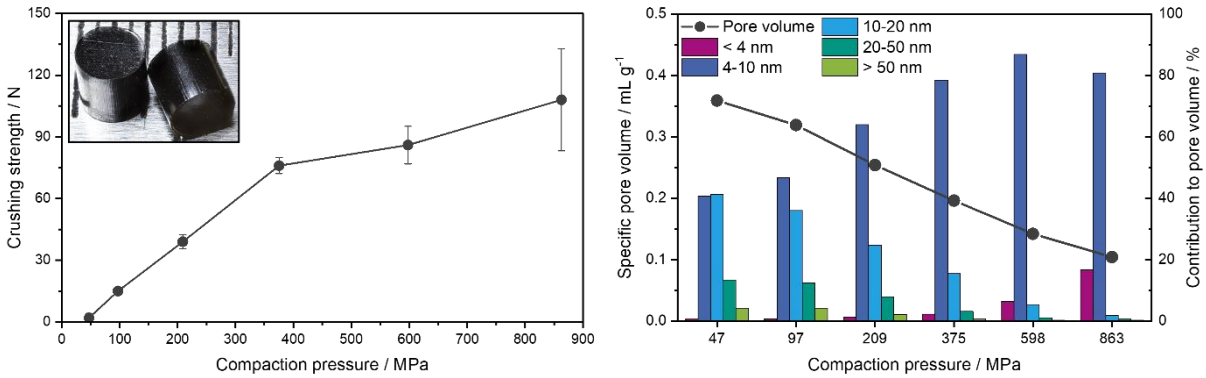


Figure 1: Crushing strength (left) and specific pore volume and contribution of different pore size ranges to the pore volume (right) of cylindrical tablets (2 x 2 mm) in dependence of compaction pressure.

The presented study shows that a moderate graphite content is necessary for a high mechanical stability, but also to have sufficient lubrication enabling continuous tablet production. Increasing the compaction pressure and tablet density exemplified the expected trade-off between mechanical stability and desirable physico-chemical properties like porosity. The results however show that with less than 50% of the highest compaction pressure investigated, similar and more reliable mechanical stabilities can be achieved while avoiding further negative effects on porosity and reducibility.

References

1. S. Mitchell, N.-L. Michels, J. Pérez-Ramírez, *Chem. Soc. Rev.* **2013**, *4*, 6094−6112.
2. J.T. García-Sánchez, V.G. Baldovino-Medrano, *Ind. Eng. Chem. Res.* **2023**, *62*, 7769−7838.
3. M. Campanati, G. Fornasari, A. Vaccari, *Catal. Today* **2003**, *77*, 299−314.
4. D. Guse, L. Warmuth, M. Herfet, K. Adolf, T.A. Zevaco, S. Pitter, M. Kind, *Catalysts* **2024**, *14*, 517−359.

Acknowledgements

The authors would like to thank Diana Deutsch from IKFT and David Guse, Florian Kreißig and Mathias Kind from the Institute of Thermal Process Engineering (TVT) at KIT for their contribution to the synthesis of the $CuO/ZnO/ZrO_2$ catalyst. The authors acknowledge Hg porosimetry measurements by Malina Burcea and Gregor Wehinger from the Institute of Chemical Process Engineering (CVT) at KIT. Financial support by the Helmholtz Research Program “Materials and Technology for the Energy Transition (MTET), Topic 3: Chemical Energy Carriers” is highly acknowledged.

Assessing the effect of catalyst structure on the competitive CO_2 hydrogenation pathways to CO and Methanol on Copper

Kaustav NIYOGI, Matteo MAESTRI*
Politecnico di Milano
Laboratory of Catalysis and Catalytic Processes, Department of Energy
Via La Masa 34, Milano 20156, Italy
**corresponding author: matteo.maestri@polimi.it*

Significance and Relevance

This work deciphers the effect of the catalyst structure on the different reaction pathways controlling the product selectivity towards methanol and carbon monoxide in copper (Cu)-based CO_2 hydrogenation. Our analysis, using atomistic modeling of detailed reaction mechanisms on different catalyst crystal facets, resolves the experimentally observed, often contradictory reports regarding the structure-dependent activity, the effect of water in accelerating the reaction rates and whether the different product pathways share common intermediates, paving the way for rational catalyst design.

Preferred and 2nd choice:CO_2 utilization and recycling,Fundamental advances in understanding catalysis
Preferred presentation: Oral / Short Oral

Introduction and Motivations

Methanol (MeOH) synthesis through CO_2 hydrogenation is regarded as a key technology to recycle waste CO_2 into valuable base chemicals closing the carbon loop[1]. However, there is still significant discrepancy in the research community on the exact kinetic mechanism behind the selectivity towards methanol/ CO, hindering the development of efficient catalysts for the process[1]. Kinetic studies have suggested that the MeOH formation and reverse water-gas shift reaction (rWGS) take place through parallel pathways with no common intermediates[2]. However, isotope tracing experiments have shown that in the presence of water or at low temperatures, methanol is primarily produced from CO, suggesting a sequential reaction mechanism[3]. Recent structure sensitivity studies have further speculated that the product pathways may vary drastically between Cu(111), Cu(100) compared to Cu(211), Cu(110) surfaces[4]. Ultra-high vacuum studies have shown that the catalytic activity can also differ by orders of magnitude between Cu facets such as Cu(111) and Cu(110), making it challenging to experimentally assess the catalyst structure effects[5]. This work uses first-principles based atomistic modeling to the shed light on different and often contradictory experimental observations regarding the methanol/ CO selectivity on Cu at operationally relevant temperature and pressure conditions.

Materials and Methods

Density Functional Theory (DFT) calculations are carried out on multiple Cu planar facets using Quantum ESPRESSO suite with GGA-PBE pseudopotentials, a plane wave basis set, Grimme D3 dispersion, represented by five-layer slabs of p(3x2) periodic unit cells with vacuum spacing of 12 Å. In total, *19 adsorbate species and 32 elementary reactions are assessed*, to address the complexity of CO and MeOH formation. Climbing-Image Nudged-elastic band calculations are used to detect the transition states. Vibrational analysis is used to determine the ZPE corrections, temperature dependent heat capacities and entropy contributions for determining the Gibbs free energies.

Results and Discussion

Fig. 1 shows the comparison between the minimum energy path for the rWGS reaction on Cu(111) and Cu(110) facets. For both the surfaces, CO production through direct CO_2 dissociation is energetically more favorable over the CO2 hydrogenation-based carboxyl route. However, our analysis shows that an alternate water-assisted CO_2 hydrogenation route exists with significantly lower activation barrier making the carboxyl pathway most energetically feasible. While such a pathway may not be observed under UHV experiments, pressurized experimental conditions may result in lowering the overall CO formation energy barrier through this route along an integral reactor. Also, Fig. 1 shows that the Cu(110) facet is energetically much more favorable towards CO formation compared to

Cu(111), due to preferential surface stabilization of the CO* and OH* adsorbates, explaining the experimental observation of the three orders of magnitude higher CO formation rates on Cu(110) compared to Cu(111), seen in UHV studies of Yoshihara et al.[3,5]

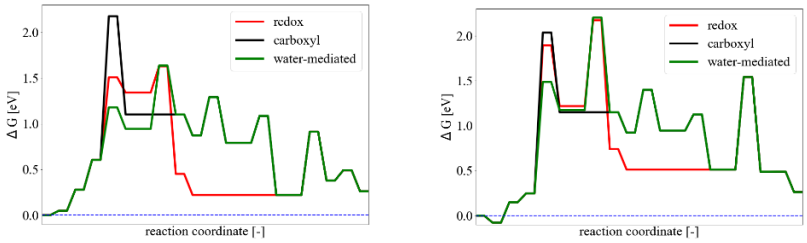


Figure 1. Free energy surface for rWGS pathways on (a) Cu(110) and (b) Cu(111), at T=528K,p=30bar with respect to the reference state: $CO_{2(g)}$+$H_{2(g)}$+$H2O_{(g)}$

The potential energy surface for the different reaction pathways towards MeOH formation are shown in Fig,2. On both the surfaces formate (HCOO*)-based pathway is the energetically most favorable, agreeing with experimental observation of high formate species coverage[3,4]. However, one interesting difference can be observed in terms of the most energy demanding steps towards MeOH formation on the different surfaces. Fig. 2(a) suggests that on Cu(110), with increasing pressures towards industrial scales (>75-90 bar), as the formate pathway opens up (ΔG becomes <0, for the shaded section), other routes remain energetically unfeasible. This stems from the lower activation barriers of water formation steps on Cu(110) and suggests a dominant HCOO*-based pathway towards MeOH formation on this surface, explaining the recent particle size effect observed by Barberis et al.[4]

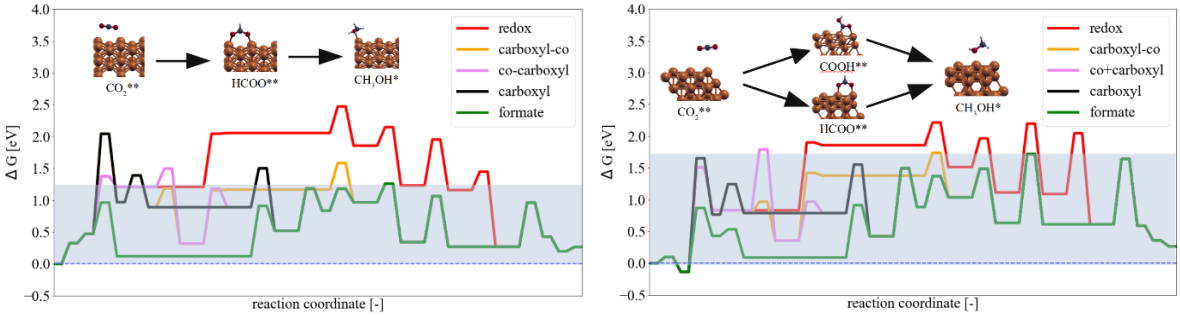


Figure 2. Free energy surface for MeOH pathways on (a) Cu(110) and (b) Cu(111), at T=528K,p=30bar with respect to the reference state: $CO_{2(g)}$+$3H_{2(g)}$

On the Cu(111) surface, on the other hand, the activation barriers towards MeOH formation are higher and appear downstream along the reaction coordinate (Fig. 2(b)). As a consequence, when the formate pathway opens up, the carboxyl (COOH*)-based pathway also becomes energetically accessible for MeOH formation. A significant consequence of this result is that on Cu(111), CO and MeOH may no longer be formed through separate parallel paths but through a common carboxyl intermediate, making it challenging for selectivity tuning by catalyst structuring for large-sized Cu nanoparticles, where Cu(111) surface dominates. Our work thus provides key fundamental insights on the coupling between different catalytic cycles on different Cu facets, paving the way for the rationalization of experimental observations of the competitive CO_2 hydrogenation on Cu.

References

1. R. Schlogl, Angew. Chem. Int. Ed., **2022**, 61, e202007397
2. T.C. Lin, A. Bhan, J. Cat., **2024**, 429, 115214.
3. Y. Yang et al., J. Cat., **2013**, 298, 10-17.
4. L. Barberis et al., Nanoscale, **2022**, 14, 13551.
5. J. Yoshihara & C.T. Campbell, J. Cat, **1996**, 367, 661–666.

Acknowledgements

Financial support from HORIZON-MSCA-2022-PF-01 Project:101106487 (UNVEIL), MUR sponsored Project: CUP D43C22003090001 (PNRR Next Generation EU - PE2-NEST) and computational time from the Italian supercomputing cluster CINECA (Bologna, Italy) are acknowledged.

Ni-DOPED TUNGSTEN CARBIDE CATALYSTS FOR THE SELECTIVE PRODUCTION OF ETHYLENE GLYCOL FROM CELLULOSIC MATERIALS

Nicola PANZA*, Marta STUCCHI, Laura PRATI
Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19 Milano Italy
**nicola.panza@unimi.it*

Significance and Relevance

The selective conversion of glucose and cellulose toward ethylene glycol formation, was successfully obtained over Ni-doped tungsten carbide catalysts supported on different carbon materials. The role of nickel and the support were established. The high yield and selectivity of EG obtained directly from cellulose and the cheapness of the catalyst, pave the way to a possible use of this materials for the conversion of more complex matrices such as paper industry waste (PPMS), with the possibility to obtain high-value added ethylene glycol in a new renewable way.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion / Circular economy
Preferred presentation: Oral preferred or short oral

Introduction and Motivations

The utilization of waste and biomass for material production presents a promising pathway, particularly regarding environmental sustainability compared to methods based on fossil resources.[1] Cellulose and cellulosic waste, such as pulp and paper mill sludge (PPMS), hold significant appeal due their abundance and non-competition with food production. Transforming these materials into valued products, like polyols, offers a fresh, sustainable source of materials, especially for commodity polymers production.[2] Traditionally, noble metal catalysts like Pt, Pd, and Ru were employed for cellulose valorization through hydrogenation reactions, but there is a strong push towards utilizing more readily available non-noble metals. Hence, we propose catalytic systems based on tungsten carbides supported on different carbon supports, combined with Ni, for the in situ hydrolysis of cellulosic waste into glucose, and subsequent selective hydrogenation to ethylene glycol.

Results and Discussion

Different Ni doped tungsten carbide catalysts were prepared and tested under different conditions in glucose or cellulose hydrogenation with the aim of optimizing ethylene glycol production. As the support we selected three different carbons, namely an activated carbon (X40S), a carbon black (Vulcan XC72) and graphene nano-platelets (GNP). The catalysts were prepared by incipient wetness impregnation and then calcined in H_2.
The catalysts were selected on the basis of their influence in balancing the different possible reaction pathways (isomerization, retroaldol, hydrogenation, degradation). The nickel presence resulted fundamental not only for the hydrogenation reaction but also for WC_2 formation, essential for promoting retroaldol reaction, i.e. first step for EG formation (Fig 1).

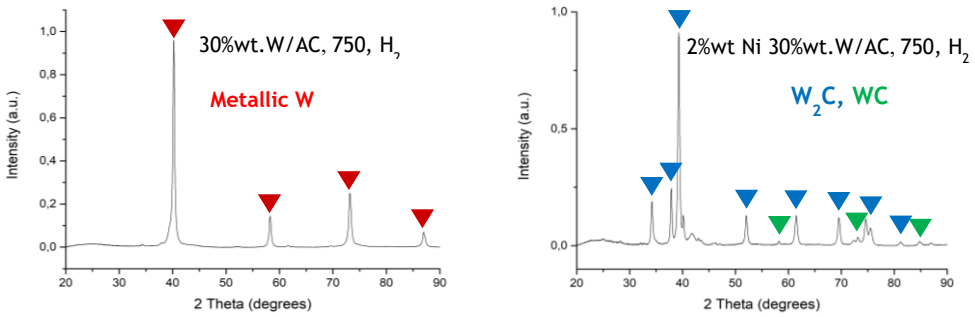


Fig 1-*XRD spectra of catalysts prepared in absence or presence of Ni, after the same calcination conditions (750°C, H_2)*

All the materials were characterized by multiple techniques such as XRD, FESEM, BET, XPS EDS. Regarding the catalytic activity, the materials in which the nickel was not present, led to the formation of undesired degradation products. The catalytic optimized conditions, for both glucose and cellulose, were found varying temperature, hydrogen pressure and reaction time. Starting from glucose a 35% yield of EG has been obtained with the catalyst supported on activate carbon (X40S) at **220°C** under **40 bar** of hydrogen for **30 minutes**. For the direct conversion of cellulose, as expected, we have to use harsher conditions due to the initial de-polymerization step, but an outstanding **51%wt** yield of EG has been obtained at **245°C** under **60 bar** of hydrogen for **2.5h**. We found that in this latter case the best catalytic performances have been obtained using the graphene nanoplates (GNP) as the support (Fig.2). We correlate this surprising result to the low local concentration of glucose deriving from the depolimerisation of cellulose thus a possible match between the kinetic of de-polymerization and the following retro-aldol condensation/hydrogenation step limiting the formation of by-products.

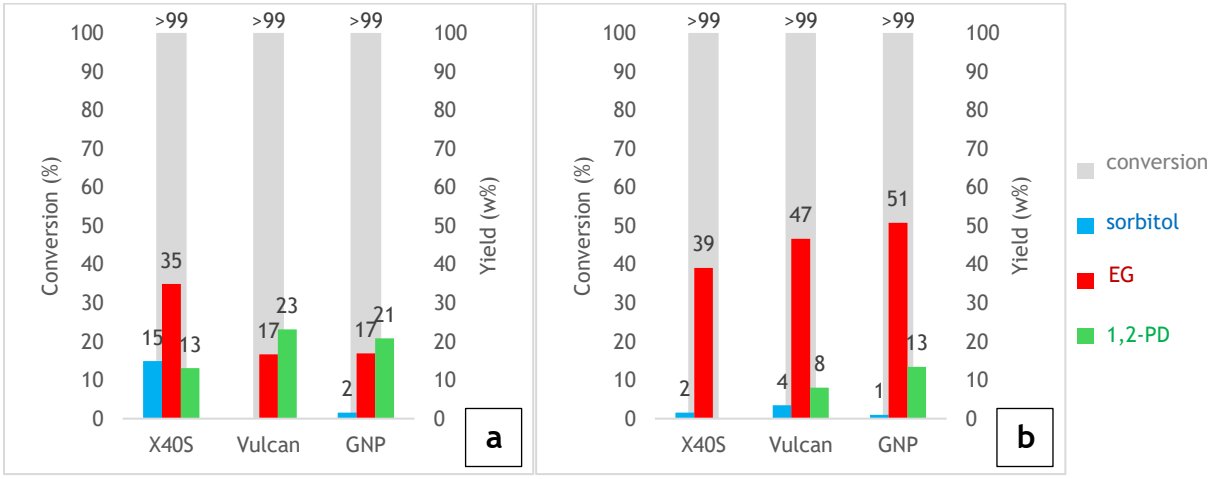


Figure 2-*Catalytic performances of the different supported catalysts on Glucose (**a**) and Cellulose (**b**)*

FESEM analysis on the spent catalysts showed in both cases (glucose and cellulose reactant) the formation of tungsten oxide WO_3, which might be derived by a partial dissolution and oxidation of the WC_2 in the reaction media. For this reason, the nature of the true active species is still to be assessed and further analysis will be performed to shed light on the role of the support.

References

1. Atsushi Fukuoka, Paresh L. Dhepe, *Angew. Chem. Int. Ed.*, **2006**, 45, 5161-5163
2. Mee Kee Wong, Serene Sow Mun Lock, Yi Herng Chan, *Chem. Eng. J.*, **2023**, 468,143699.

Acknowledgement

This work is part of the project REWAMP: EFFECTIVE RECYCLING OF CELLULOSIC WASTE FROMPAPERINDUSTRY, funded by PRIN 2022 PNRR-M4C2 investment line 1.1
Project code: P202282F9N

Structure-Activity Evolution of $AgNbO_3$ via Exsolution

Amy Radford[1], Nathan Coltart[1], Yiyang Li[1*], Edman Tsang[1]
[1]*Wolfson Catalysis Centre, University of Oxford, Oxford, England*
*yiyang.li@chem.ox.ac.uk

Significance and Relevance

Exsolution is a technique of industrial significance which facilitates the formation of stable catalyst heterostructures. Using a model perovskite, $AgNbO_3$, this work expands understanding of how the structure-activity relationship develops for photocatalytic dye degradation during exsolution. Using an array of characterization techniques, focusing on both the labile Ag^+ cations and static Nb^{5+} cations, a picture is being built of the structural development during thermal exsolution.

Preferred and 2nd choice for the topic: Photocatalysis and photoelectrocatalytic approaches, solar energy utilization
Fundamental advances in understanding catalysis

Preferred presentation: Poster

Introduction and Motivations

Exsolution is an excellent approach to designing highly active and stable perovskite photocatalyst heterostructures.[1] Under reduction conditions, labile metal cations are drawn from the bulk to the perovskite surface where they coalesce to form nanoparticles (NPs). These NPs are strongly embedded within the surface, improving their stability compared to standard deposition techniques. For $AgNbO_3$, exsolution leads to Ag NP formation.[2] In photocatalysis, Ag NPs are known to act as plasmonic co-catalysts, enhancing light interaction and charge carrier lifetime of semiconductor photocatalysts.[3] The effect of Ag-exsolution on $AgNbO_3$ photocatalytic activity is multi-modal, through: perovskite surface reforming, changing bulk structure, and Ag NP co-catalyst formation.

Materials and Methods

$AgNbO_3$ synthesized by grinding Ag_2O and Nb_2O_5 in a 1:1 molar ratio, then calcining under O_2 at 900 ^oC for 5 hrs. The perovskite was exsolved under 5% H_2/N_2 at 400 ^oC for 15, 30, or 45 mins. Product characterizations: XRD, UV-vis DRS, SEM, STEM-EDX, TPR, TRPL, XPS.

Photocatalytic degradation of Rhodamine B dye (40 mL, 5 mg L^{-1}) using $AgNbO_3$ (40 mg) was performed under irradiation of a 500 W UV lamp for 3 hrs. Dye concentration was determined from the relative absorption (λ_{RhB} = 554 nm) using UV-vis spectroscopy.

Results and Discussion

$AgNbO_3$ was successfully exsolved to form a $Ag/AgNbO_3$ heterostructure. Under reduction using 5% H_2 at 400 ^oC, Ag^+ cations were removed from the perovskite bulk and formed Ag^0 NPs on the surface. SEM images of samples which underwent 0, 15, 30, and 45 mins of exsolution clearly show an increase in the surface coverage of NPs. Initially, NPs formed at grain boundaries and in surface ridges, then arose in areas of lower surface energy, and eventually covered the entire perovskite surface. UV-vis DRS data confirms the NP's Ag^0 composition from characteristic absorption peaks in the 400-600 nm region which increase in intensity alongside exsolution time. XRD, XPS and STEM-EDX analyses reinforce this conclusion.

The fate of the Nb^{5+} cations has been less clear. XRD analysis cannot identify any changes to the perovskite structure, however curious shifting in the Nb 3d XPS indicates the Nb coordination number may be changing from 6-to-5-to-6 as the structure is exsolved. To probe the Nb changes

further, *in-situ* XAS analysis is being pursued; this technique will also allow for a kinetic assessment of Ag^+ movement through the perovskite structure. Understanding the Nb coordination environment will give a fuller picture on the bulk structure evolution.

Dye degradation tests of the photocatalyst series revealed a volcano trend between photocatalytic performance and extent of exsolution (Fig. 1). Considering just the Ag^0 formation, the initial increase in Ag^0 surface coverage (0 to 30 mins) likely improved catalytic performance because the NPs were acting as plasmonic co-catalysts. The steep drop in activity after 30 mins could be explained by an over-production of Ag^0 NPs blocking the $AgNbO_3$ surface from light absorption and blocking active sites from dye-interaction. Changes to the perovskite structure will also have contributed to the catalytic activity. During reduction, oxygen vacancy formation is expected which can aid performance in small numbers – by acting as electron sinks which delay electron-hole recombination – but in large numbers can be detrimental to fast charge carrier movement. The role Nb plays is under investigation and is the final part needed for full comprehension of the structure-activity relationship.

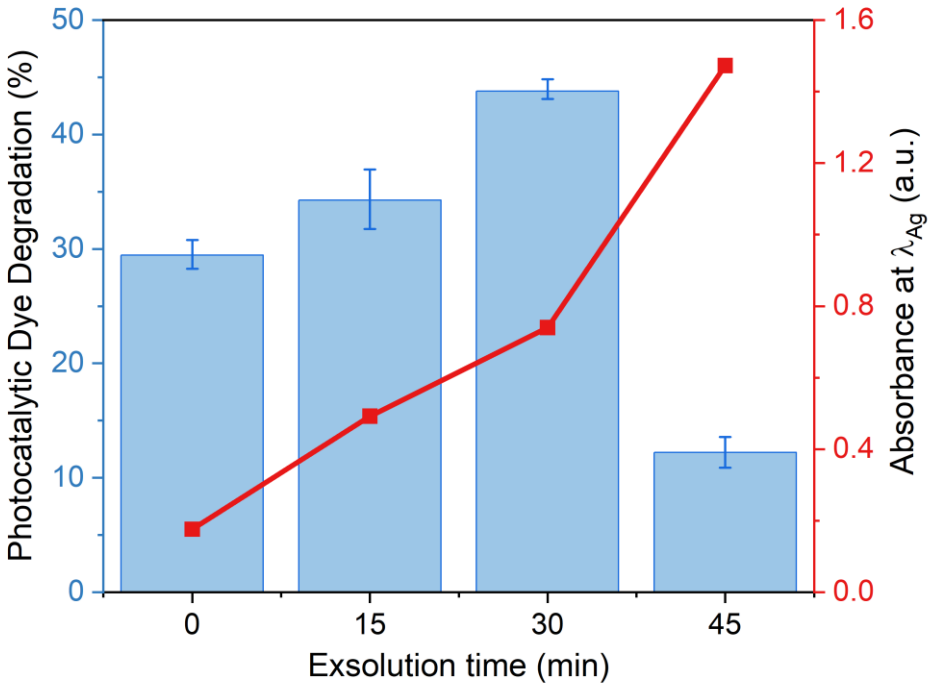


Figure 1. Graph showing effect of exsolution time on $AgNbO_3$ photocatalytic dye degradation of Rhodamine B and on Ag NP surface coverage (indicated by UV-vis DRS Ag (λ_{Ag}: 400-600 nm)).

References

1. K. Kousi, C. Tang, I. S. Metcalfe and D. Neagu, *Small*, **2021**, *17,* 2006479
2. X. Li, L. Dai, Z. He, W. Meng, Y. Li, L. Wang, *Sens. Actuat. B: Chemical*, **2019**, *298,* 126854
3. S. Linic, P. Christopher, D. Ingram, *Nat. Mater.*, **2011**, *10,* 911

TiN based Single-Atom Catalyst in Aqueous Environment: a Step Towards the Experimental Complexity

Clara SAETTA[1], Giovanni DI LIBERTO[2], Gianfranco PACCHIONI[3]
[1,2,3]*Università degli Studi Milano-Bicocca, Department. of Materials Science, Via Roberto Cozzi 55, Milan, Italy.*
[1] *c.saetta@campus.unimib.it*

Significance and Relevance

This work shows that solvation significantly influences the interfacial behavior of TiN-based Single Atom Catalysts (SACs). Using ab initio molecular dynamics, we show that water strongly adsorbs on bare TiN, forming a structured interface. Introducing platinum into nitrogen or Titanium vacancies enhances water dissociation and alters interfacial charge distributions. These findings highlight the dynamic solvent effects on SAC reactivity, providing novel insights into Pt@TiN's catalytic potential and advancing the understanding of aqueous-phase SAC behavior in real-world applications.

Preferred and 2nd choice for the topic: Fundamental advances in understanding catalysis; Multiscale modeling and advanced simulation aspects.
Preferred presentation: Poster

Introduction and Motivations

Catalysis has a key role in the green transition, it is fundamental in most of the industrial processes that we need to redefine in order to invert the trends in climate change. Single atom catalysts(1) are now emerging as a hot topic. They bridge homogeneous and heterogeneous catalysis by unifying their advantages, providing higher yield with lower metal loading. The basic problem related with these systems is that one needs simulation to approach their atomistic nature. In the modeling phase, many aspects are left behind, such as the role of unconventional intermediate and the impact of solvation.(2–5) In this work we present a study on solvation of TiN bare surface and the corresponding two Single Atom Catalysts one can form introducing Pt in either N vacancy or Ti vacancy. Platinum supported on TiN is a promising system. It is important to evaluate the dynamic effect of the solvent because its presence can change the shape and the structure of the active site and therefore its reactivity. To access this information we used ab-initio molecular dynamics.(4,6) This can lead to a deeper understanding of the Pt@TiN SACs in aqueous environment which can be explained by the interactions between the catalyst's surface and the solvent. With this work we are not only aiming at describing the behavior of a novel catalyst in aqueous environment, but we are also attempting to make a further step towards the experimental complexity.

Results and Discussion

Ab-initio molecular dynamics (AIMD) simulations of the TiN-water interface reveal significant differences in interfacial behavior depending on surface modifications. Starting from bare TiN, water molecules exhibit strong adsorption to surface titanium atoms, forming a stable hydration layer, as one can see in *Figure 1*. The effect of the Nitrogen comes into play when one considers dissociated water on the surface, we can see that a water molecule close to the surface can donate a proton to an exposed nitrogen generating an hydroxyl group. This interaction significantly affects the surface electronic properties by inducing local charge redistribution. When a Platinum atom is introduced into either a Nitrogen or Titanium vacancy, the interfacial chemistry changes. For the Pt@N-vacancy, platinum acts as a catalytic site, enhancing water dissociation and increasing the formation of hydroxyl species at the interface. Similarly, for the Pt@Ti-vacancy, the platinum atom promotes stronger interactions with water molecules, but the vacancy influences the charge distribution differently, affecting the dynamics of water reorientation and dissociation. These findings highlight the potential of Pt@TiN surfaces for applications in catalysis and electrochemical systems, as the introduction of Pt significantly modifies the interfacial structure and reactivity compared to bare TiN.

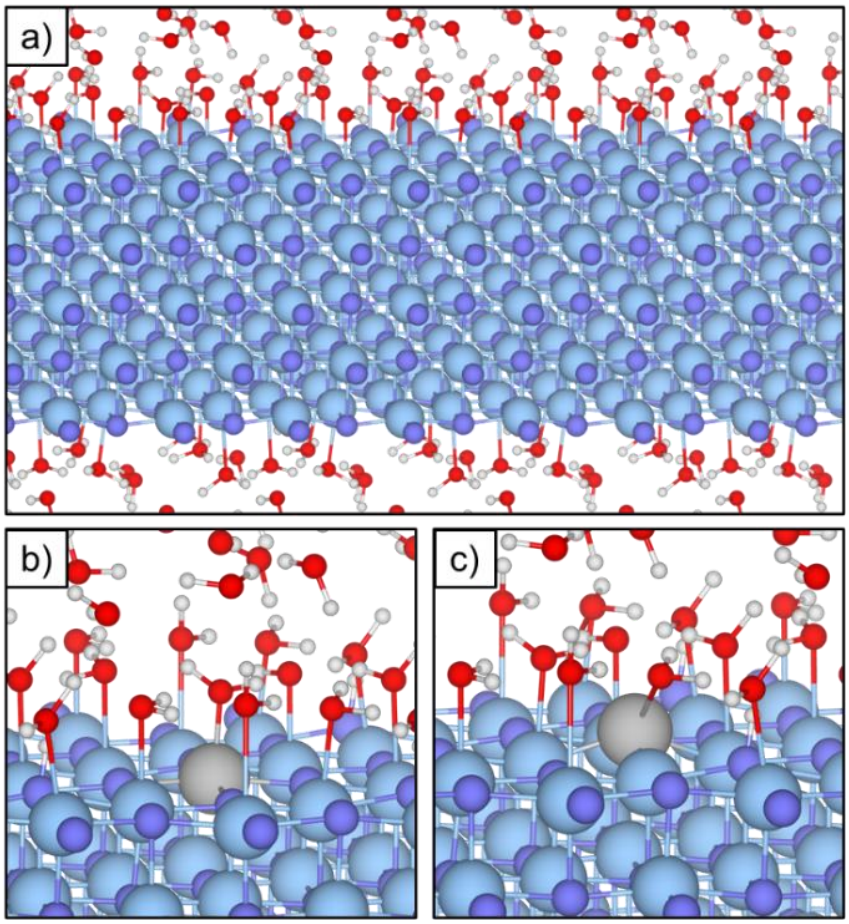


Figure 1: a) Snapshot of water/Ti_xN_x interface during AIMD calculation; b) Snapshot of water/Pt@$Ti_{x-1}N_x$ interface during AIMD calculation; c) Snapshot of water/Pt@Ti_xN_{x-1} interface during AIMD calculation.

References

1. Yang XF, Wang A, Qiao B, Li J, Liu J, Zhang T. Single-atom catalysts: A new frontier in heterogeneous catalysis. Acc Chem Res. **2013** Aug 20;46(8):1740–8.
2. Saetta C, Di Liberto G, Pacchioni G. Water Splitting on a Pt1/C3N4 Single Atom Catalyst: A Modeling Approach. Top Catal. **2023** Sep 1;66(15–16):1120–8.
3. Saetta C, Barlocco I, Liberto G Di, Pacchioni G. Key Ingredients for the Screening of Single Atom Catalysts for the Hydrogen Evolution Reaction: The Case of Titanium Nitride. Small. **2024** Sep 1;20(37):2401058.
4. Di Liberto G, Pacchioni G, Shao-Horn Y, Giordano L. Role of Water Solvation on the Key Intermediates Catalyzing Oxygen Evolution on RuO2. The Journal of Physical Chemistry C. **2023** Jun 1;127(21):10127–33.
5. Di Liberto G, Cipriano LA, Pacchioni G. Role of Dihydride and Dihydrogen Complexes in Hydrogen Evolution Reaction on Single-Atom Catalysts. J Am Chem Soc. **2021** Dec 8;143(48):20431–41.
6. He Z Da, Hanselman S, Chen YX, Koper MTM, Calle-Vallejo F. Importance of Solvation for the Accurate Prediction of Oxygen Reduction Activities of Pt-Based Electrocatalysts. Journal of Physical Chemistry Letters. **2017** May 18;8(10):2243–6.

CO_2 Purification of Industrial Flue Gas: The Role of Copper and Carbonate Species in the Selective Catalytic Reduction Process.

Abou Rahhal A.[1], Genty E.[1], Cousin R.[1], Ponchel A.[2], Noel S.[2], Poupin C.[1], Siffert S.[1]*
[1]*Univ. Littoral Côte d'Opale, UR 4492, UCEIV, Unité de Chimie Environnementale et Interactions sur le Vivant, F-59140, Dunkerque, France*
[2]*Univ. Artois, CNRS, Centrale Lille, Univ. Lille, UMR 8181, Unité de Catalyse et de Chimie du Solide (UCCS), rue Jean Souvraz, SP 18, 62300 Lens, France*
**stephane.siffert@univ-littoral.fr*

Significance and Relevance

The redox treatments performed for cobalt-copper based catalyst significantly enhanced the catalytic performance of the selective catalytic reduction (SCR) of industrial flue gas. Analytical techniques underlined that Cu^{2+}/Cu^{+} species and mono- and polydentate carbonates are key parameters for the catalytic efficiency and selectivity under oxidative and wet conditions. This work emphasizes the novel role of carbonate and copper species for enhancing SCR performance to offer a low-cost alternative to noble metal catalysts in the purification of CO_2.

Preferred and 2nd choice for the topic: Fundamental advances in understanding catalysis - Air cleaning and combustion.
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

In recent decades, environmental and human health have become a critical concern due to various atmospheric pollutants mainly greenhouse gases such as CO_2. Therefore, it is essential to minimize the amount of CO_2 released to the atmosphere by carbon capture facilities for either its utilization or storage[1]. Industrial flue gas is composed of various gases, primarily CO_2, combined with other pollutants mainly NO and CO that are harmful to environment and human, as well as oxygen and water vapor[2]. Consequently, and prior to CO_2 valorization, CO_2 purification is a crucial step to remove both NO and CO using selective catalytic reduction process based on the following reaction: $NO + CO \rightarrow CO_2 + ½\ N_2$. Transition metal-based catalysts have shown competitive results compared to noble metals being less expensive[3]. In addition, recent study underlined the effect of various thermal gas treatments (Air, He, 1% CO/He, and CO_2) for copper-based catalysts revealing its impact on the catalytic activity of SCR process[4]. The aim of this study is to synthesize cost effective and efficient copper and cobalt based catalyst, emphasizing the role of various thermal gas treatments and its impact on NO SCR by CO of industrial flue gas under oxidative and wet conditions.

Materials and Methods

Cobalt-copper based layered double hydroxide structures were synthesized by precipitating respective amounts of metal nitrates over sodium carbonate solution maintaining a constant pH using sodium hydroxide. The solution was set to age (maturation step) under room temperature and then filtered, washed and dried to obtain CoCuAl LDH samples.

These samples were thermally treated under different gas atmosphere at 400 °C to obtain the respective mixed oxide (CoCuAl Air or CO_2 samples). Subsequent redox cycles ($CO\text{-}O_2$ or $CO\text{-}CO_2$) were performed to promote the formation of specific Cu active sites denoted as CoCuAl Air $CO\text{-}O_2$ for example. The redox treated samples were then characterized by various techniques including X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. Catalytic tests were conducted in a

continuous-flow reactor under simulated flue gas conditions (20.5% CO_2, 8.8% O_2, 8.2% H_2O, with 1300 ppm of CO and 500 ppm of NO) at temperatures ranging from 100 to 400 °C.

Results and Discussion

The redox treatment performed on CoCuAl mixed oxides demonstrated lower temperature of total CO oxidation at 240 and 260 °C (Figure 1). XRD analysis revealed crystallographic phases of CuO and Cu_2O species within redox treated samples that are responsible for the enhancement of CO oxidation. The $Co_4Cu_2Al_2$ Air R CO-O_2 sample showed enhanced NO reduction compared to the air treated sample reaching 31% of N_2 yield at 320 °C with the highest selectivity of 56% (Figure 1). When comparing NO reduction temperatures, both redox treated samples exhibited lower temperature of reduction compared to the air treated sample where TG and FTIR analysis confirmed the presence of mono and polydentate carbonates that play a primary role for NO reduction. Based on further characterization (XPS, Raman …), the relationship between catalytic activity and the role of copper and/or carbonate species will be clearly defined.

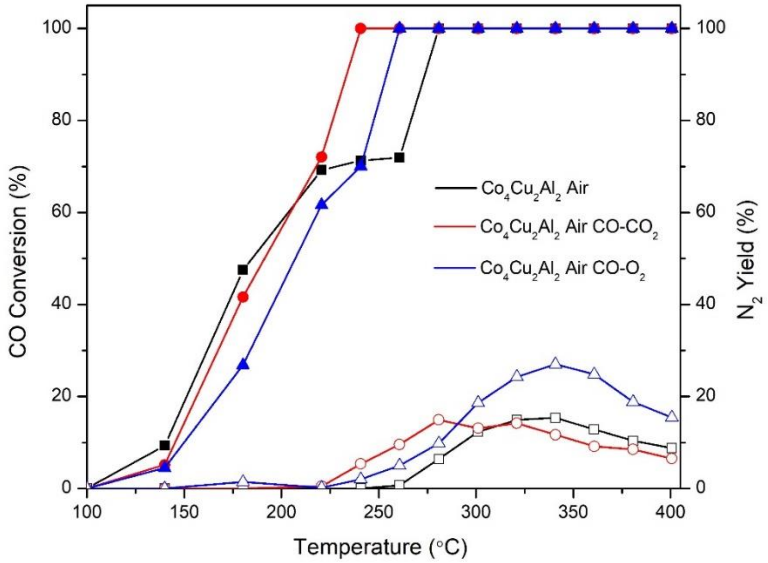


Figure 1. CO conversion and N_2 yield for $Co_4Cu_2Al_2$ air and subsequent redox treated samples as function of reaction temperature.

Acknowledgements

The authors would like to thank the PIA Dunkerque l'Energie Créative and Université du Littoral Côte d'Opale as well as MatHyBioCat project and CPER BiHautsEcodeFrance for their financial support to this research work.

References

1. J. Ma, L. Li, H. Wang et al. *Engineering*. 2022, *14*, 33–43.
2. I. Larki, A. Zahedi et al. *Sci. Total Environ*. 2023, *903*, 166108.
3. S. Liu, J. Gao et al. *J. Chem. Eng*. 2024, *486*, 150285.
4. M. Behera,S. Royer, et al. *Chem. Eng*. 2023, 452, 139543.

Sustainable synthesis of ketals from ethyl levulinate and glycerol

Francesco TADDEO[*,1], Rosa VITIELLO[1], Rosa TURCO[1], Riccardo TESSER[1], Vincenzo RUSSO[1], Martino DI SERIO[1]
[1]*University of Naples Federico II, Chemical Sciences Department, Via Cintia, Napoli, Italy.*
** francesco.taddeo@unina.it*

Significance and Relevance

The use of renewable sources offers significant environmental and health benefits by replacing fossil-derived products with sustainable chemicals from biomass. Among these, ketals derived from levulinic acid and its derivatives have emerged as promising compounds with several applications, including fuel additives, plasticizers, solvents, and precursors for biopolyol and polyurethane synthesis. This study explores the catalytic synthesis of ketals, comparing the performance of various catalysts to identify those with the best characteristics. A kinetic investigation was conducted in both batch and continuous reactors, providing the data for a possible future scale-up of the process.

Preferred and 2nd choice for the topic: 1. Green Chemistry and biomass transformation, renewable resources conversion; 2. Circular economy.
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster): Oral only

Introduction and Motivations

The development of sustainable chemical processes through biomass valorization is a key strategy to replace fossil derived chemicals with renewable alternatives. In this context, levulinic acid and its derivatives play an important role.[1] Among these, ethyl levulinate can be considered a particularly attractive compound, derived from biomass based raw material and ethanol, combining low production costs with the use of renewable resources. This makes it a valuable precursor for further chemical transformations. Glycerol, a by-product of biodiesel production, contributes to the sustainability of the process by enabling industrial waste valorization. The advantages in using the esters, such as ethyl levulinate, can be found in avoiding the occurrence of the competitive esterification reaction. The ketalization of ethyl levulinate with glycerol produces ketals, versatile compounds with numerous industrial applications, due to their valuable properties. It involves the formation of a five-membered ketal as the main product, in addition to a six-membered ketal and water.[2] Catalysis plays a fundamental role in this process, and both homogeneous catalysts (e.g., mineral acids) and different heterogeneous catalysts are commonly employed. While homogeneous catalysts often ensure high conversions, heterogeneous catalysts offer significant environmental and operational advantages, including reusability, resistance to high temperatures, and simplified recovery processes.[3] This study focuses on the kinetic investigation of ethyl levulinate ketalization with glycerol in the presence of heterogeneous catalysts. A catalytic screening was made in order to identify those with the most promising properties, followed by kinetic studies. Experiments were conducted in both batch and continuous reactors to explore the effect of operating conditions on reaction rates to provide data useful for the possible scale-up of the process.

Materials and Methods

The kinetic batch experiments were performed in a 0.3 L Hastelloy reactor under varying conditions of temperature, stirring rate, ethyl levulinate/glycerol molar ratio and catalyst loading. For continuous experiments, a milli-reactor 8 cm long with an internal diameter of 0.3 cm, packed with the heterogeneous catalyst, was employed. In the continuous setup experiments were made at different temperatures and volumetric flowrates. Samples were analyzed through ^{1}H-NMR in order to evaluate the reached conversion.

Results and Discussion

The ketalization of ethyl levulinate with glycerol was investigated through a comprehensive screening of various catalytic systems in order to identify the most promising ones. Kinetic investigations were performed in a batch reactor, varying the operative conditions to assess their influence on the reaction rate. Among the tested catalysts, Strata-XL-C showed outstanding performance. Experiments were performed by varying stirring rate to evaluate the possible presence of the fluid-solid mass transfer resistance, while temperature variation allowed the determination of activation energy and reaction enthalpy, obtaining higher conversions at higher temperatures, confirming the endothermicity of the reaction. The ethyl levulinate/glycerol molar ratio was varied to investigate its influence on the reaction rate and on the thermodynamic plateau, and catalyst loading to assess the contribution of autocatalysis and the effect of the catalyst on the initial reaction rate. With increased catalyst loading, equilibrium was achieved in a short time, less than 10 minutes, highlighting the catalyst efficiency. Continuous experiments were conducted in a milli-reactor under varying temperatures and flow rates to verify the process feasibility in continuous operation, collecting data useful for model validation.

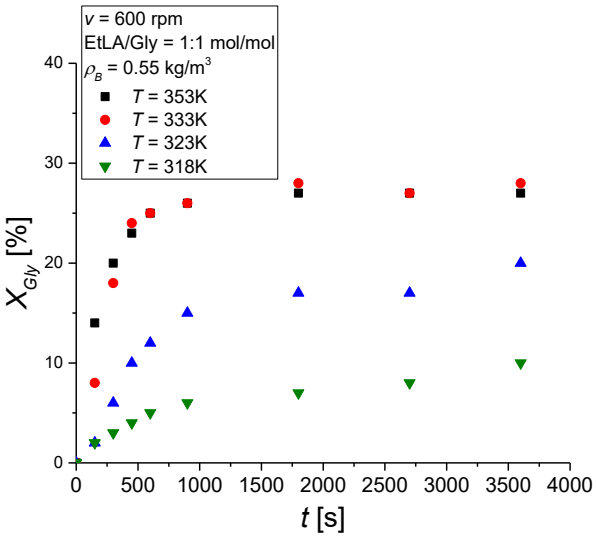


Figure 1 Temperature effect for experiments promoted by Strata-XL-C fixing, v = 600 rpm, ρ_B = 0.55 kg/m^3, EtLA/Gly = 1:1 mol/mol.

References

1. R.A. Sheldon, *Green Chem.* **2014**, *16*, 950–963.
2. F. Taddeo, R. Tesser, M. Di Serio, V. Russo, *Chem. Eng. Process. - Process Intensif.* **2024**, *197*, 109712.
3. A.S. Amarasekara, M.A. Animashaun, *Catal. Lett.* **2016**, *146*, 1819–1824.

Acknowledgements

Thanks are due to the Circular and Sustainable Made in Italy Extended Partnership (MICS) funded by the European Union Next-Generation EU (Piano Nazionale di Ripresa e Resilienza (PNRR) - Missione 4, Componente 2, Investimento 1.3 - D.D. 1551.11-10-2022, PE00000004) for financial support.

Synthesis and Characterization of Nickel Cobalt Catalysts

Gitana Valeckytė, Zita Sukackienė, Jūratė Vaičiūnienė, Loreta Tamašauskaitė-Tamašiūnaitė, Eugenijus Norkus
Department of Catalysis, Center for Physical Sciences and Technology (FTMC),
Saulėtekio al. 3, LT-10257 Vilnius, Lithuania
gitana.valeckyte@ftmc.lt

Significance and Relevance

The production of high-purity hydrogen from hydrogen storage materials with further direct use of generated hydrogen in fuel cells is still a relevant research field. For this purpose, nickel cobalt-plated copper catalysts (NiCo/Cu), comprising between 4 and 90 wt.% cobalt, as catalytic materials for hydrogen generation, were prepared using a low-cost, straightforward electroless metal deposition method by using citrate plating baths, a metal source and morpholine borane as a reducing agent. The catalytic activity of the prepared NiCo/Cu catalysts toward alkaline sodium borohydride (NaBH4) hydrolysis increased with the increase in the content of cobalt present in the catalysts.

Preferred and 2nd choice for the topic: Sustainable and clean energy production and transport; H2 storage and transportation, green H2 production, hydrogen vectors
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster) *Poster*

Introduction and Motivations

Hydrogen is a good alternative to coal, oil and natural gas [1]. The reason we need to replace fossil fuels is that they are constantly depleting, and when burned, the products of such fuels pollute the environment and cause the greenhouse effect, thus contributing to climate change. Although the majority of hydrogen is produced from natural gas (62 %), coal (19 %), or naphtha reforming (18 %), it can be change. Extremely pure hydrogen is obtained during the borohydride hydrolysis reaction, which can be directly used as a hydrogen fuel cell. In addition, fuel cells using pure hydrogen emit almost no pollutants other than water [2].

Materials and Methods

The aim of this work was to identify NiCo(4)/Cu, NiCo(10)/Cu, NiCo(20)/Cu, NiCo(80)/Cu and NiMo(90)/Cu catalysts, characterize them and evaluate their catalytic properties for sodium borohydride for the hydrolysis reaction. All NiCo coatings were deposited on a Cu substrate by a simple chemical deposition method using morpholine borane as a reducing agent. Catalysts were obtained with different cobalt mass percentages: 4, 10, 20, 80 and 90. The surface morphology, structure and chemical composition of the catalysts were investigated using scanning electron microscopy (SEM) and induced plasma optical emission spectroscopy (ICP-OES). The catalytic effect of the sodium borohydride hydrolysis reaction was evaluated by measuring the amount of hydrogen present in the catalyzed borohydride hydrolysis reaction.

Results and Discussion

During the work, all the mentioned NiCo/Cu catalysts were formed. Their morphology and structure were investigated. It was established that the prepared coatings consist of particles of various sizes that are combined into oval-shaped agglomerates. It was found that the two-component NiCo/Cu with 90 mass percent exhibited the highest catalytic activity. This catalyst was found to have an activation energy of 52.5 kJ/mol and an H_2 evolution rate of 1.46 mL/min at 30 °C and 15.61 mL/min at 70 °C. The synergetic effect between nickel and cobalt, in addition to the formation of solid-state solutions between metals, promoted the hydrogen generation reaction.

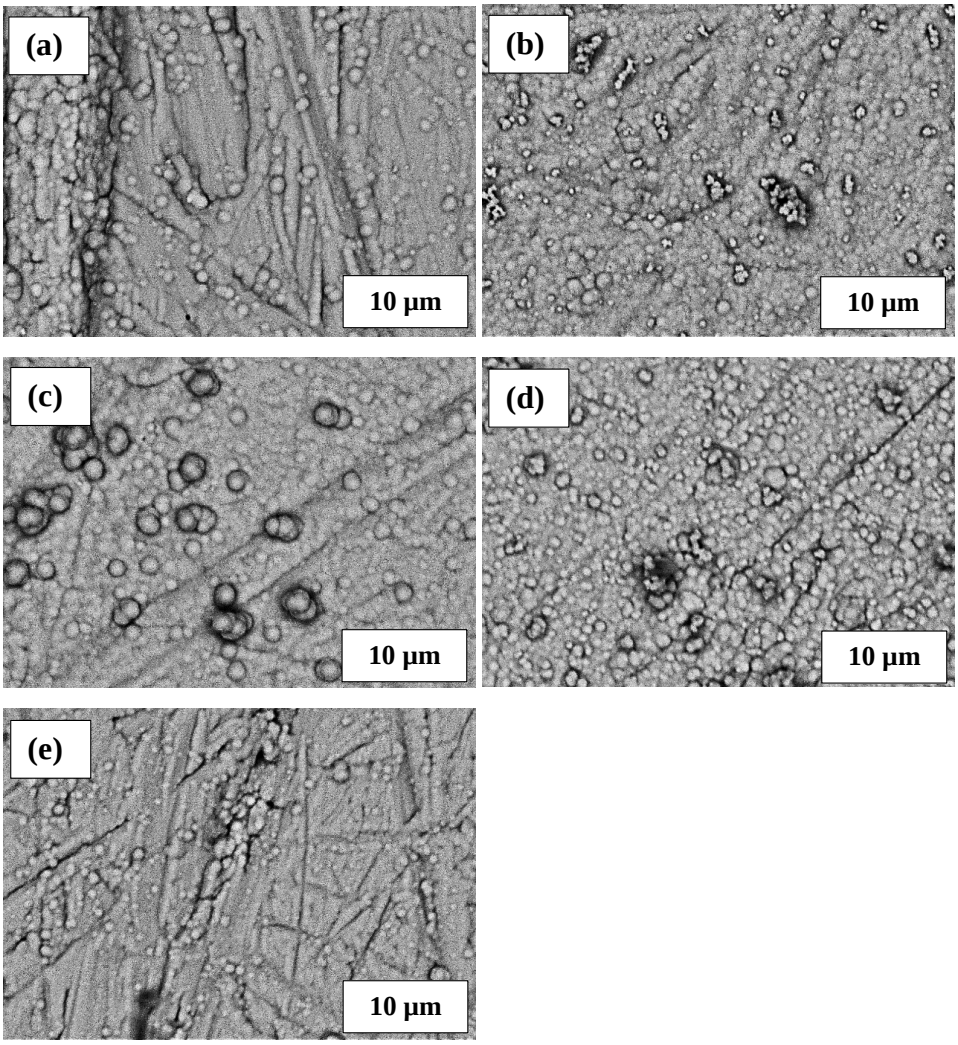


Figure 1 SEM images of prepared NiCo(4)/Cu (a), NiCo(10)/Cu (b), NiCo(20)/Cu (c), NiCo(80)/Cu (d) and NiCo(90)/Cu (e)

References

1. F. Alasali, M.I. Abuashour, W. Hammad, D. Almomani, A.M. Obeidat, W. Holderbaum, *Energy Science and Engineering.* **2024**, *12*, 1934–1968.
2. L. Van Hoecke, L. Laffineur, R. Campe, P. Perreault, S. W. Verbruggen, S. Lenaerts, *Energy and Environmental Science*, **2021**, *14*, 815-843.

Acknowledgements

Research Council of Lithuania for funding of grant.

Nanofiber-reinforced composite Proton-Exchange Membranes

Michele Zanoni[1], Elyes Bel Hadj Jrad[1,2], Elisabetta Petri[1,2], Francesca Soavi[1,2], Chiara Gualandi[1]

[1]Dept. of Chemistry "Giacomo Ciamician", University of Bologna, Via Selmi 2, 40126, Bologna, Italy
[2]Centre for the Environment, Energy, and Sea - Interdepartmental Centre for Industrial Research in Renewable Resources, Environment, Sea and Energy (CIRI-FRAME), University of Bologna, Viale Ciro Menotti 48, 48122, Marina di Ravenna, Italy

c.gualandi@unibo.it

Significance and Relevance

This work aims to develop innovative proton exchange membranes (PEMs) with superior performance compared to traditional membranes based on Nafion. This study is focused on Aquivion-based membranes reinforced with electrospun fibers produced using different types of polymers, including polyvinylidene fluoride (PVDF) and sulfonated poly ether ether ketone (SPEEK). Results indicate that thinner membranes improve proton conductivity while keeping good mechanical properties.

Preferred topic: H_2 storage and transportation, green H2 production, hydrogen vectors
Preferred presentation: Poster

Introduction and Motivations

New proton exchange membranes, made by Aquivion[1] and reinforced with electrospun fibers, are developed and characterized in this study to find the optimal formulation to enhance RFB performance by balancing efficiency and reducing self-discharge[2].

Materials and Methods

Membranes were fabricated using Aquivion reinforced with three types of electrospun supports: PVDF, organic-inorganic hybrid of PVDF copolymer and SiO_2, and SPEEK. The membranes were characterized using advanced techniques such as scanning electron microscope (SEM), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), stress-strain tests, water uptake measurements, and proton conductivity and area-specific resistance (ASR) by impedance spectroscopy (EIS). These properties were analyzed to assess efficiency and chemical stability.

Results and Discussion

In this work, we present the results of using the fabricated Aquivion-based membranes with different types of electrospun reinforcement materials to highlight their respective advantages and limitations. The discussion focuses on the mechanical and chemical stability of the membranes and their proton conductivity. The influence of membrane composition, thickness, and reinforcement strategy on the transport properties is analyzed, along with the role of water uptake in facilitating proton transport and its correlation with the type of reinforcement material used. The morphology of the membranes, particularly the integration of the electrospun mats and their impact on structural stability, is examined in detail and related to their proton transport behaviour.

References

1. P. Xiong, L. Zhang, Y. Chen, S. Peng, G. Yu. *Angew. Chem. Int. Ed.*, **2021**, *60*, 24770.
2. J. Choi, K. M. Lee, R. Wycisk, P. N. Pintauro, and P.T. Mather. *Macromolecules*, **2008**, 41, 13.

Acknowledgements

This work was supported by the MIAMI Project 2022-2025 - Italian Minister for Ecological Transition, MiTE codice proposta CSEAA_00014

Nanofiber-reinforced composite Proton-Exchange Membranes

Michele Zanoni[1], Elyes Bel Hadj Jrad[1,2], Elisabetta Petri[1,2], Francesca Soavi[1,2], Chiara Gualandi[1]

[1]Dept. of Chemistry "Giacomo Ciamician", University of Bologna, Via Selmi 2, 40126, Bologna, Italy
[2]Centre for the Environment, Energy, and Sea - Interdepartmental Centre for Industrial Research in Renewable Resources, Environment, Sea and Energy (CIRI-FRAME), University of Bologna, Viale Ciro Menotti 48, 48122, Marina di Ravenna, Italy

c.gualandi@unibo.it

Significance and Relevance

This work aims to develop innovative proton exchange membranes (PEMs) with superior performance compared to traditional membranes based on Nafion. This study is focused on Aquivion-based membranes reinforced with electrospun fibers produced using different types of polymers, including polyvinylidene fluoride (PVDF) and sulfonated poly ether ether ketone (SPEEK). Results indicate that thinner membranes improve proton conductivity while keeping good mechanical properties.

Preferred topic: H_2 storage and transportation, green H2 production, hydrogen vectors
Preferred presentation: Poster

Introduction and Motivations

New proton exchange membranes, made by Aquivion[1] and reinforced with electrospun fibers, are developed and characterized in this study to find the optimal formulation to enhance RFB performance by balancing efficiency and reducing self-discharge[2].

Materials and Methods

Membranes were fabricated using Aquivion reinforced with three types of electrospun supports: PVDF, organic-inorganic hybrid of PVDF copolymer and SiO_2, and SPEEK. The membranes were characterized using advanced techniques such as scanning electron microscope (SEM), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), stress-strain tests, water uptake measurements, and proton conductivity and area-specific resistance (ASR) by impedance spectroscopy (EIS). These properties were analyzed to assess efficiency and chemical stability.

Results and Discussion

In this work, we present the results of using the fabricated Aquivion-based membranes with different types of electrospun reinforcement materials to highlight their respective advantages and limitations. The discussion focuses on the mechanical and chemical stability of the membranes and their proton conductivity. The influence of membrane composition, thickness, and reinforcement strategy on the transport properties is analyzed, along with the role of water uptake in facilitating proton transport and its correlation with the type of reinforcement material used. The morphology of the membranes, particularly the integration of the electrospun mats and their impact on structural stability, is examined in detail and related to their proton transport behaviour.

References

1. P. Xiong, L. Zhang, Y. Chen, S. Peng, G. Yu. *Angew. Chem. Int. Ed.*, **2021**, *60*, 24770.
2. J. Choi, K. M. Lee, R. Wycisk, P. N. Pintauro, and P.T. Mather. *Macromolecules*, **2008**, 41, 13.

Acknowledgements

This work was supported by the MIAMI Project 2022-2025 - Italian Minister for Ecological Transition, MiTE codice proposta CSEAA_00014

Book of Abstract. 13th International Conference on Environmental Catalysis (ICEC 2025)

© 2025 Brussels, Belgium by ERIC aisbl Press

https://www.eric-aisbl.eu/

ISBN 979-12-210-9763-4

