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

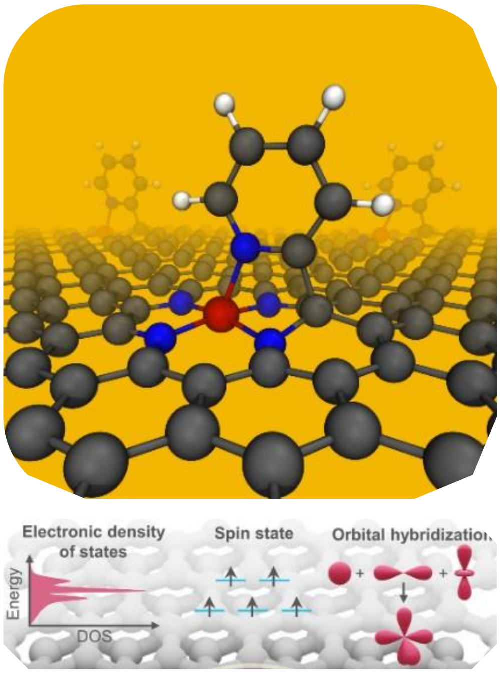
This study provides detailed insights into the impact of axial ligand modifications on the reactivity and selectivity of Fe-based single-atom catalysts (SACs) for CO_2 reduction reactions (CO_2RR). A key finding is that all examined axial ligands, including chloride, 2-aminopyridine, and 8-aminoquinoline, 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