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.

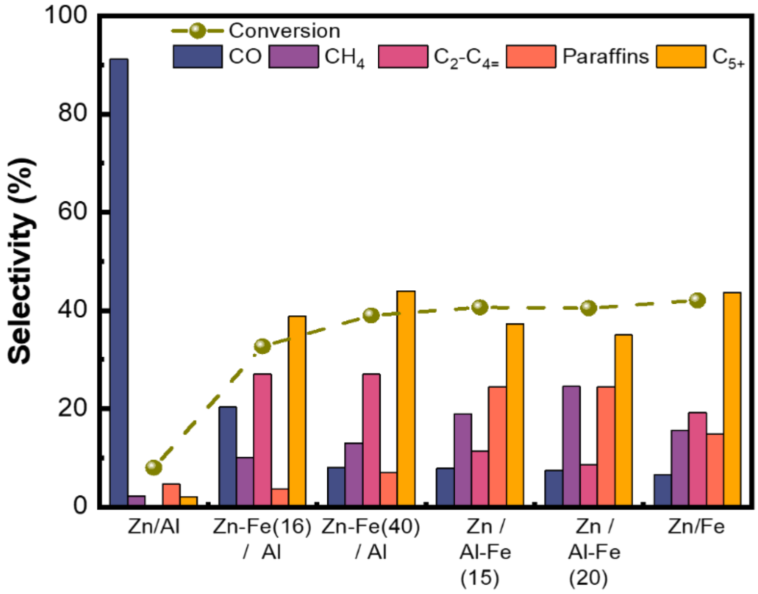

Figure 1. Conversion of CO_2 towards light olefins over Fe-based mixed oxides.

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).