Enhanced CO_2 Hydrogenation to Hydrocarbons via SIL-Modified Fe-Ru/Al_2O_3 Catalysts: Tailoring Activity and Selectivity Through Support Engineering

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Significance and Relevance

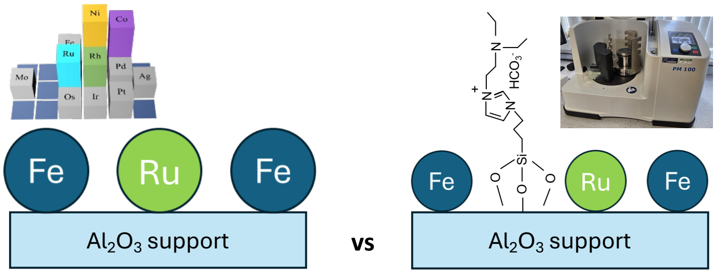
This study highlights the significance of modifying Al_2O_3 supports with supported ionic liquids (SILs) to enhance the catalytic performance of Fe-Ru-based catalysts for CO_2 hydrogenation to produce short-chain hydrocarbons when compared to the conventional colloidal synthesis approach. This work marks 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.

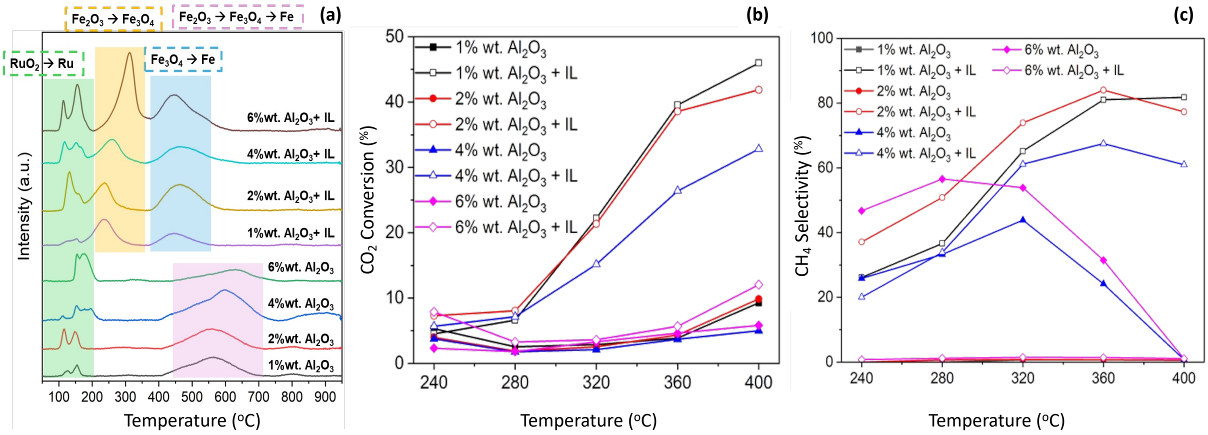


Figure 1. (a) TPR profiles (hydrogen consumption) of the prepared catalysts, Catalytic activity comparison of the samples: **(b)** CO_2 conversion, and **(c)** CH_4 selectivity respectively.

References

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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.