

Ionic Liquid Synthesis of Catalysts for Direct CO₂ Hydrogenation to short-chain hydrocarbons

Marina Maddaloni¹, Ander Centeno-Pedraza², Simone Avanzi¹, Nayan Jyoti Mazumdar², Hareesh Manyar² and Nancy Artioli^{1*}

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

*nancy.artioli@unibs.it

Introduction

The direct conversion of carbon dioxide into lower olefins (C₂-C₄) is a highly desirable process as a sustainable production route^{1,2}. These lower olefins, such as ethylene, propylene, and butenes, are crucial components in the chemical industry and for Liquefied Petroleum Gas (LPG). The reaction proceeds via two main consecutive reactions: Reverse Water Gas Shift (RWGS) to produce CO followed by the further conversion of CO to hydrocarbons via the Fischer-Tropsch reaction³. Recent studies^{4,5} highlight the cost-effectiveness and satisfactory performance of Fe-based catalysts in both reaction steps, while exploring bimetallic catalysts, particularly Ru and Fe combinations, to enhance olefin selectivity⁶, with precise MNP synthesis as a crucial factor for performance control. The study introduces a novel approach for synthesizing iron-ruthenium bimetallic catalysts that utilizes ionic liquids as solvents⁷, ensuring precise and uniform distribution of active metal phases. Advanced characterizations and extensive tests reveal that this method surpasses traditional colloid-based techniques, resulting in superior selectivity for target hydrocarbons.

Materials and Methods

In the conventional colloidal synthesis (COL) process⁶, Ru nanoparticles (Ru-NPs) were produced by a modified Schlenk technique using Ru₃(CO)₁₂ and oleylamine at 543 K. Similarly, Fe nanoparticles were synthesized from oleylamine and Fe(acac)₃ at 573 K. Bimetallic Ru-Fe nanoparticles were prepared in hexane, serving as a reference. In the ionic liquid (IL) assisted method, [BmIm][BF₄] was used with either Fe(acac)₃ or Ru₃(CO)₁₂, at temperatures of 523 K for 18 hours. Nanoparticles were recovered, and for bimetallic Fe-Ru NPs, three different molar ratios were examined (1:1, 3:1, and 9:1) using Fe(acac)₃ and Ru₃(CO)₁₂ in [BmIm][PF₆] at 523 K for 18 hours. The nanocatalysts were supported on γ-Al₂O₃ with varying metal loadings (1 or 4 wt.%). Characterization included XRF, XRD, SEM, and H₂ chemisorption. Kinetic experiments were performed at 593 K and 6 or 20 bar pressures, adjusting the gas-hourly space velocity (GHSV) to maintain CO₂ conversion below 5%, and FT-IR gas analysis was used to analyze yield and selectivity.

Results and Discussion

In Figure 1, H₂-TPR profiles of Fe₂O₃-RuO₂ catalysts prepared via different methods (COL) and IL) were analyzed to investigate their redox performance. Both sets of catalysts displayed two reduction peaks corresponding to the reduction of Fe₂O₃ to Fe₃O₄ (620K), of Fe₃O₄ to FeO(800 K) and further to Fe⁰(900 K) (Figure 1.A). The addition of RuO₂ resulted in lower

temperature reduction peaks, indicating accelerated Fe species reduction and hydrogen spillover from Ru to Fe₂O₃. The ionic liquid method exhibited differences, with the absence of a pronounced peak related to the reduction of Ru⁴⁺ to Ru⁰ (380 K). Varying Fe:Ru ratios in the ionic liquid catalysts showed that the reduction peak diminishes when ruthenium's reduction takes precedence, indicating improved reducibility through increased cooperativity between Fe and Ru species due to their closer proximity.

The variations in reducibility observed in the TPR experiment are consistent with the differences in catalytic activity. Notably, when comparing catalysts of the same composition prepared using both COL and IL methods, there was a notable five-fold increase in CO₂ conversion under 20 bar pressure. Furthermore, increasing the total metal loading from 1wt% to 4wt% significantly improved selectivity for CH₄ and C₂-C₅ hydrocarbons (Figure 1.B).

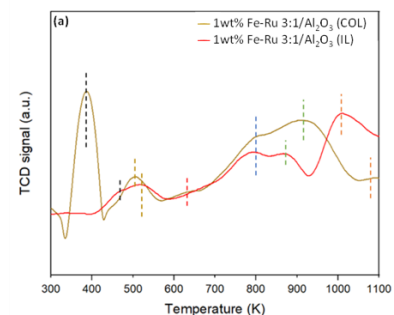


Figure 1.A H₂-TPR profiles of catalysts 1 wt% Fe-Ru 3:1/Al₂O₃ (COL and IL)

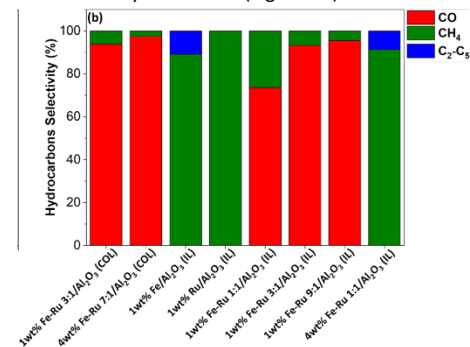






















Figure 1.B hydrocarbon selectivity at 20 bar (3:1 H₂:CO₂, 523 K)

Significance

In summary, this research effectively illustrates the improved synergy between bimetallic Fe-Ru species synthesized using the IL method, leading to superior performance and selectivity for 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 CO₂ into net-zero e-fuels for transportation and using CO₂ as a carbon feedstock for renewable resource development.

References

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