



## Ionic Liquid-Assisted Synthesis of Fe-Ru Bimetallic Catalysts for Enhanced CO<sub>2</sub> Conversion to Lower Olefins with High Selectivity

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### 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<sub>2</sub> conversion efficiency, creating pathways for sustainable applications such as the production of carbon-neutral e-fuels and the use of CO<sub>2</sub> as a renewable carbon source.

*Preferred and 2<sup>nd</sup> choice for the topic:*

*1<sup>st</sup> choice: Sustainable and clean energy production and transport;*

*2<sup>nd</sup> choice: CO<sub>2</sub> utilization and recycling.*

*Preferred presentation: Oral preferred or Short Oral*

### Introduction and Motivations

The direct conversion of carbon dioxide into lower olefins (C<sub>2</sub>-C<sub>4</sub>) offers a promising sustainable production pathway<sup>1,2</sup>. 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<sup>3</sup>. 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<sup>4,5</sup>.

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<sub>2</sub> conversion.

### Materials and Methods

In the ionic liquid (IL)-assisted method, [BmIm][BF<sub>4</sub>] was combined with either Fe(acac)<sub>3</sub> or Ru<sub>3</sub>(CO)<sub>12</sub> 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<sub>2</sub>O<sub>3</sub> with metal loadings of either 1 wt.% or 4 wt.%. The catalysts were characterized using XRF, XRD, SEM, and H<sub>2</sub> chemisorption. Kinetic experiments were conducted at 593 K and 20 bar.

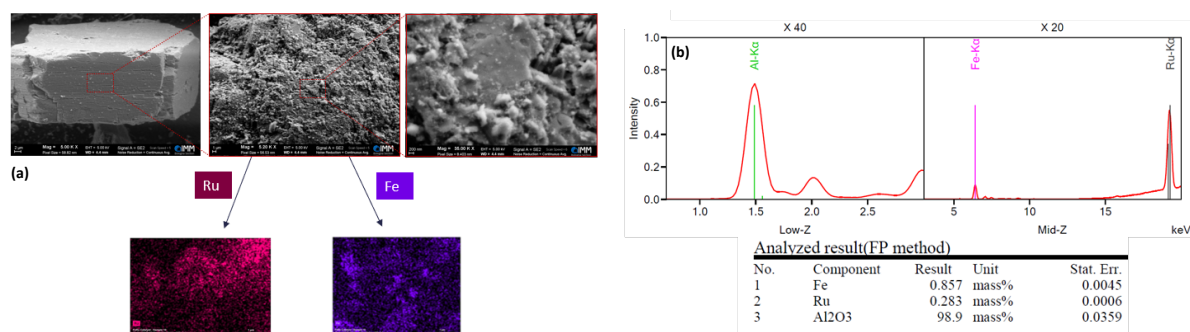
### Results and Discussion

Fe<sub>2</sub>O<sub>3</sub>-RuO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts synthesized using ionic liquid (IL) methods were analyzed through SEM and XRF to confirm the homogeneous distribution of nanoparticles (NPs) on the Al<sub>2</sub>O<sub>3</sub> support and verify the targeted Fe/Ru ratio (**Figure 1**).

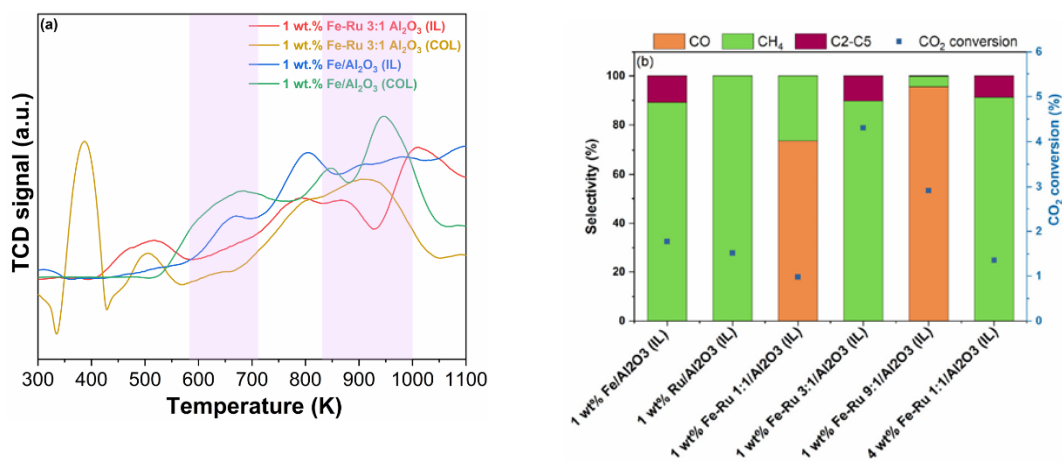
The redox properties of catalysts prepared by both traditional colloidal (COL) and IL methods were investigated via TPR (**Figure 2a**) for Fe and Fe/Ru catalysts. Both catalyst sets exhibited two distinct

reduction steps:  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$  (620 K),  $\text{Fe}_3\text{O}_4$  to  $\text{FeO}$  (800 K), and further reduction to  $\text{FeO}$  and  $\text{Fe}^0$  (900 K). The inclusion of  $\text{RuO}_2$  lowered the reduction temperature, indicating enhanced reduction of Fe species and hydrogen spillover from Ru to  $\text{Fe}_2\text{O}_3$ . The IL method revealed distinct behavior, with no noticeable peak corresponding to the reduction of  $\text{Ru}^{4+}$  to  $\text{Ru}^0$  (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  $\text{CO}_2$  conversion compared to the colloidal one. Additionally, increasing the metal loading from 1 wt% to 4 wt% significantly enhanced selectivity for  $\text{CH}_4$  and  $\text{C}_2\text{-C}_5$  hydrocarbons.



**Figure 1.** a) SEM-EDX analysis of the 1wt% Fe-Ru 3:1/ $\text{Al}_2\text{O}_3$  (IL) sample. b) XRF analysis of the 1wt% Fe-Ru 3:1/ $\text{Al}_2\text{O}_3$  (IL) sample.



**Figure 2.** a) Comparison of the TPR profiles of the 1wt% Fe-Ru 3:1/ $\text{Al}_2\text{O}_3$  IL and COL catalysts. b)  $\text{CO}_2$  conversion (%) and selectivity for IL catalysts at 20 bar and 45 mL/min.

## References

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