Ionic Liquid Synthesis of Catalysts for Direct CO_2 Hydrogenation to Short Chain Hydrocarbons

Marina Maddaloni[1], Ander Centeno-Pedrazo[2], Simone Avanzi[1], Nayan Jyoti Mazumdar[2], Juan José Villora-Picó[2]*, Haresh Manyar[2] and Nancy Artioli[1]*

j.villorapico@qub.ac.uk, nancy.artioli@unibs.it

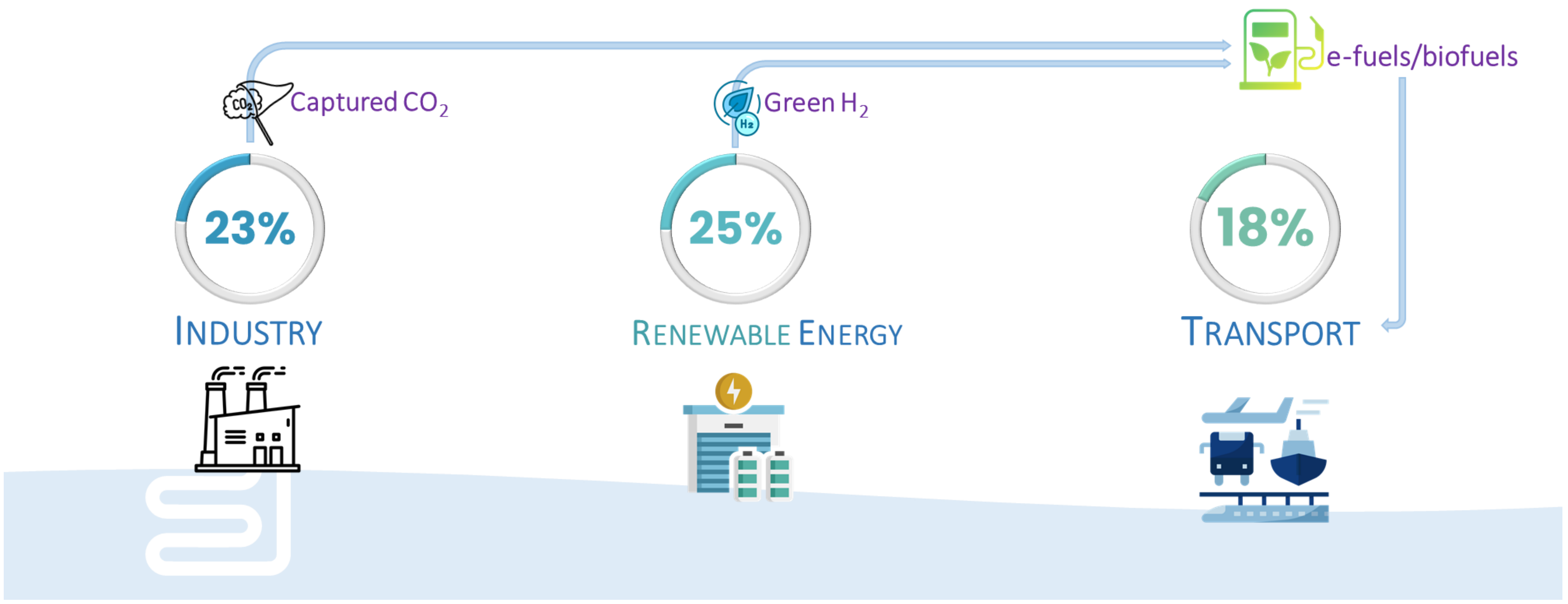
[1]CEEP Laboratory, Department of Civil Engineering, Architecture, Territory, Environment and Mathematics, University of Brescia, via Branze 38, 25123 Brescia, Italy;
[2]School of Chemistry and Chemical Engineering, Queen's University Belfast, David-Keir Building, Stranmillis Road, Belfast, BT9 5AG, UK

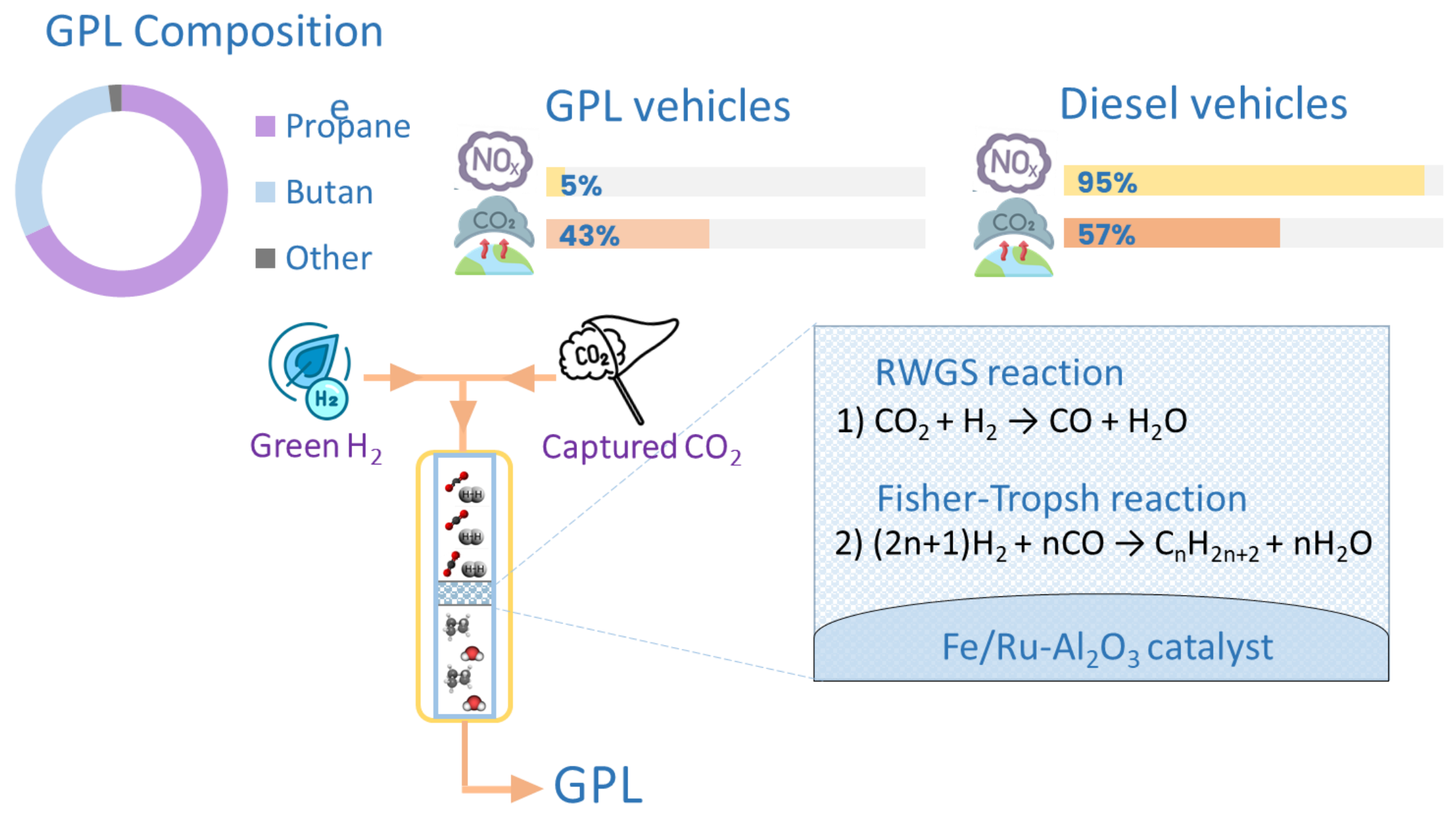
ABSTRACT

The direct conversion of carbon dioxide into lower olefins (C_2-C_4) is a highly desirable process as a sustainable production route[1]. These lower olefins, such as ethylene, propylene, and butanes, are crucial components in the chemical industry and for **L**iquefied **P**etroleum **G**as (**LPG**). The reaction proceeds via two main consecutive reactions: **R**everse **W**ater **G**as **S**hift (**RWGS**) to produce CO followed by the further conversion of CO to hydrocarbons via the Fischer–Tropsch reaction[2]. Recent studies[3] 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 selectivity[4], with precise metal nanoparticles (MNP) synthesis as a crucial factor for performance control.

OBJECTIVE

The study introduces a novel approach for synthesizing iron-ruthenium bimetallic catalysts that utilizes ionic liquids as solvents, 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.





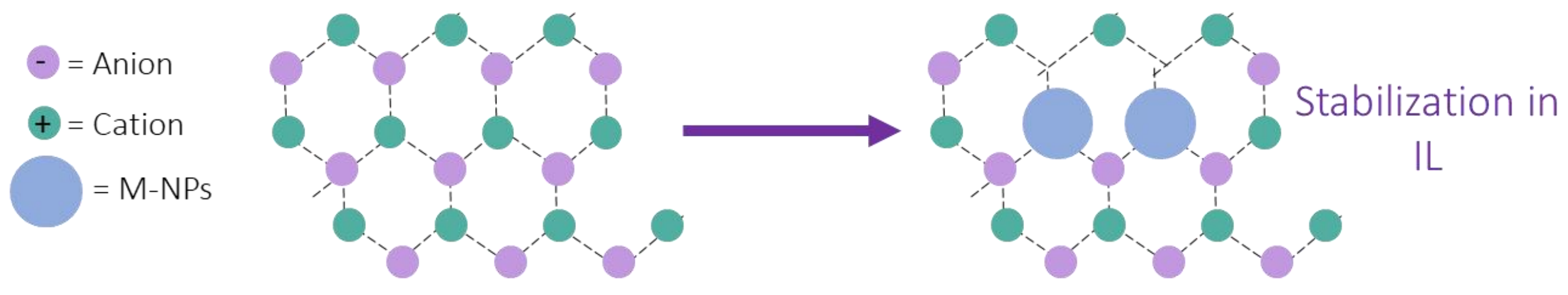
RWGS reaction
1) $CO_2 + H_2 \rightarrow CO + H_2O$

Fisher-Tropsh reaction
2) $(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O$

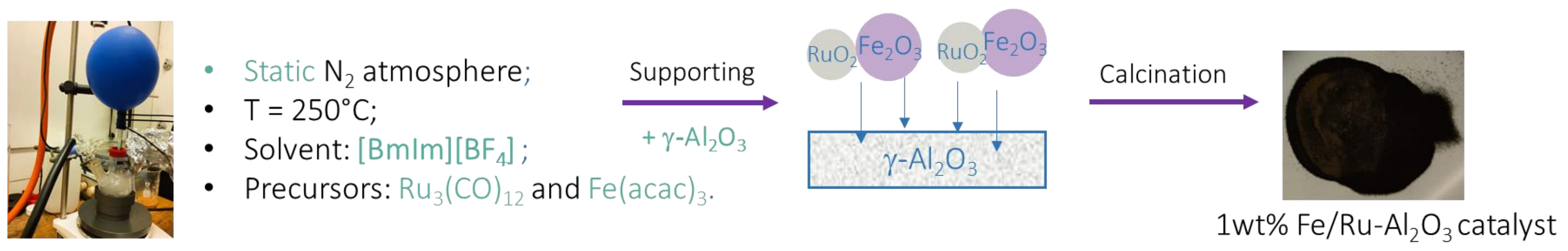
Fe/Ru-Al_2O_3 catalyst

IONIC LIQUID SYNTHESIS

1 METHODOLOGY



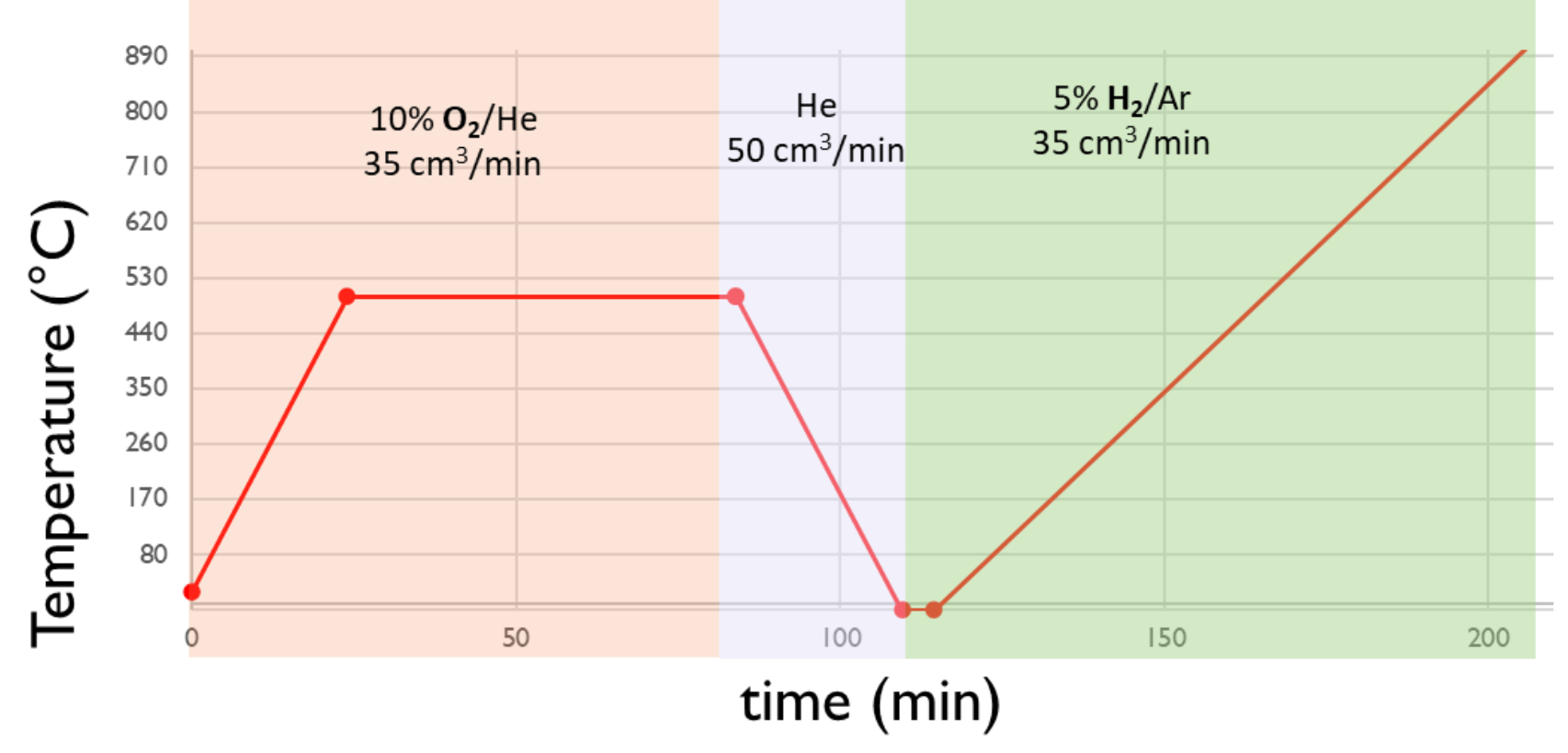
- High ionic charge;
- Strong polarity;
- High dielectric constant;
- Recyclable.



- Static N_2 atmosphere;
- T = 250°C;
- Solvent: [BmIm][BF_4] ;
- Precursors: $Ru_3(CO)_{12}$ and $Fe(acac)_3$.

1wt% Fe/Ru-Al_2O_3 catalyst

H$_2$-TPR METHOD



2 CHARACTERIZATION

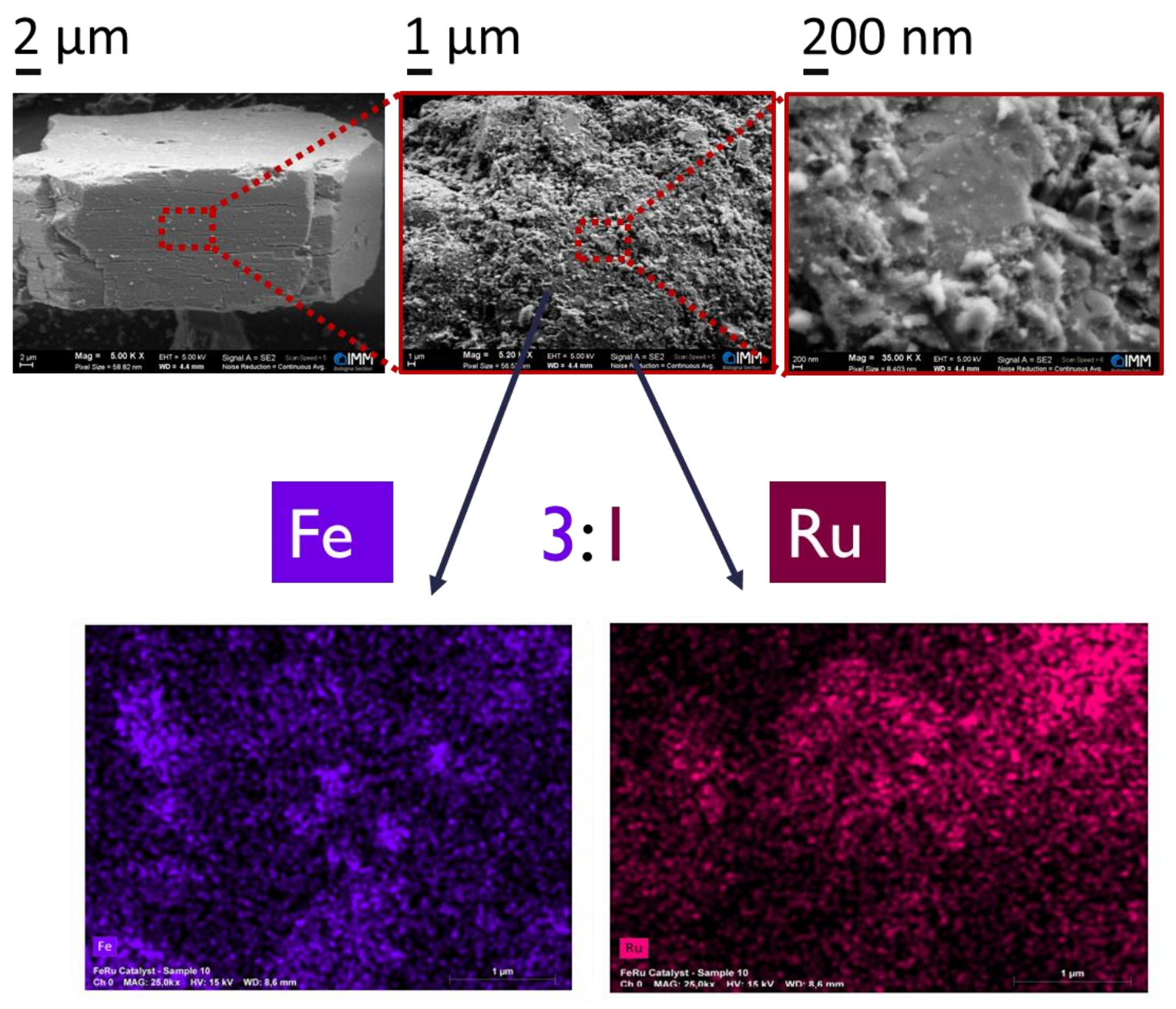


Figure 1. SEM-EDX analysis of the 1wt% Fe-Ru 3:1/Al_2O_3 (IL) sample.

Table 1. BET and XRF results of prepared catalysts.

Catalyst Name	BET		XRF (wt. %)
	Surface Area (m^2/g)	Pore Size (Å)	
1 wt.% Fe–Ru 1:1/Al_2O_3 (COL)	88.46	84.95	Fe 0.57 Ru 0.67
1 wt.% Fe–Ru 3:1/Al_2O_3 (COL)	109.44	86.81	Fe 0.7 Ru 0.27
1 wt.% Fe–Ru 9:1/Al_2O_3 (COL)	90.17	87.95	Fe 1.13 Ru 0.10
1 wt.% Fe–Ru 1:1/Al_2O_3 (IL)	86.14	97.34	Fe 0.6 Ru 0.7
1 wt.% Fe–Ru 3:1/Al_2O_3 (IL)	93.79	88.08	Fe 0.98 Ru 0.29
1 wt.% Fe–Ru 9:1/Al_2O_3 (IL)	112.23	91.72	Fe 0.88 Ru 1

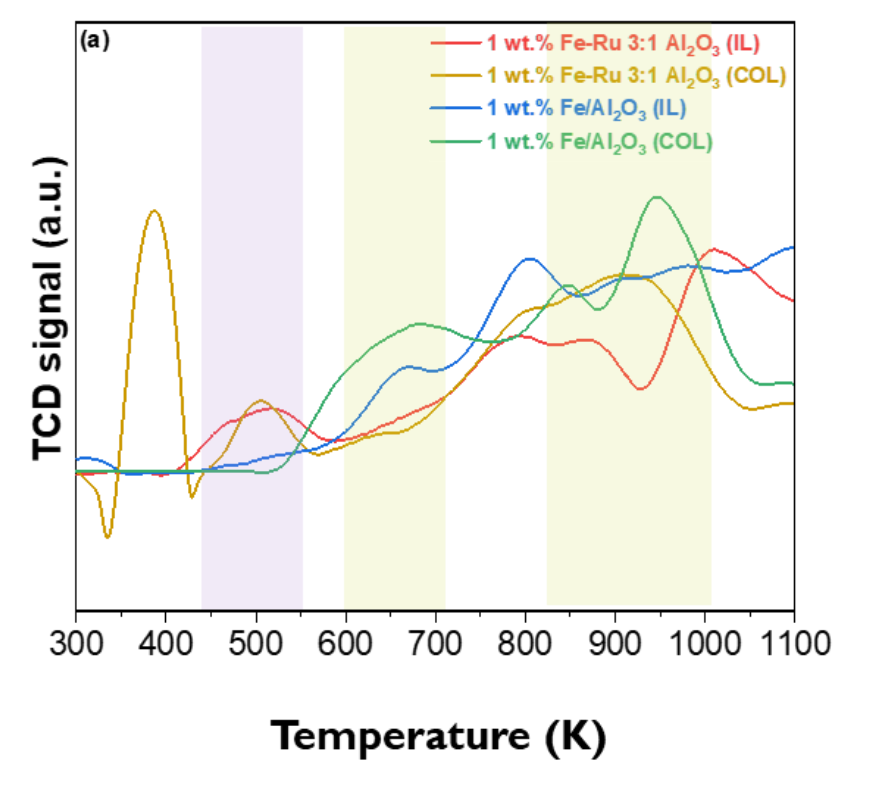


Figure 2a. TPR profiles of 1wt% Fe-Ru 3:1/Al_2O_3 catalysts prepared by IL and COL methods

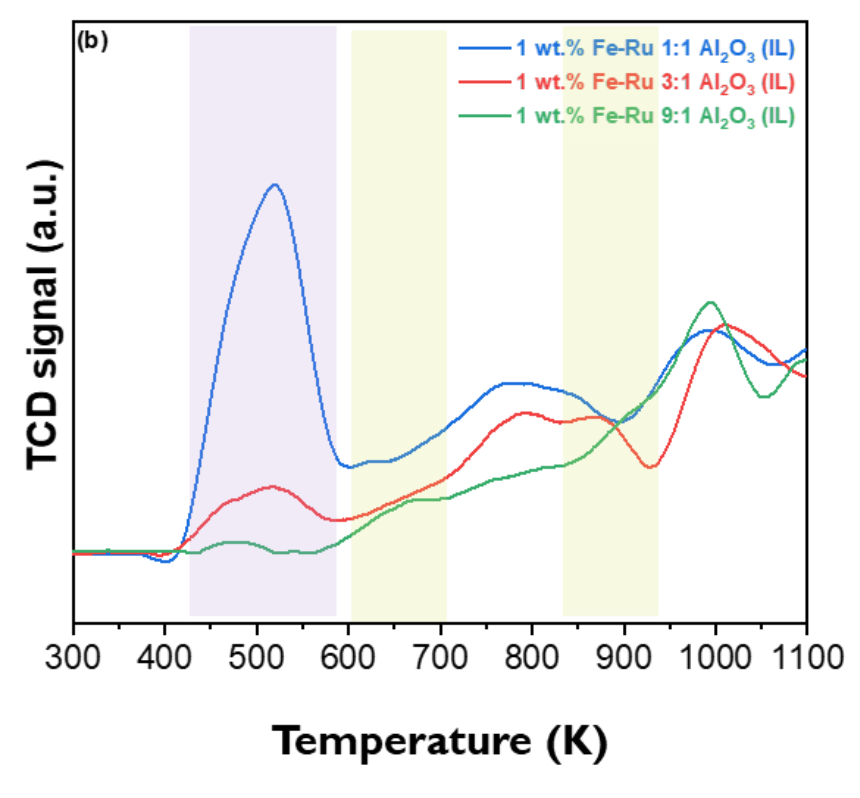
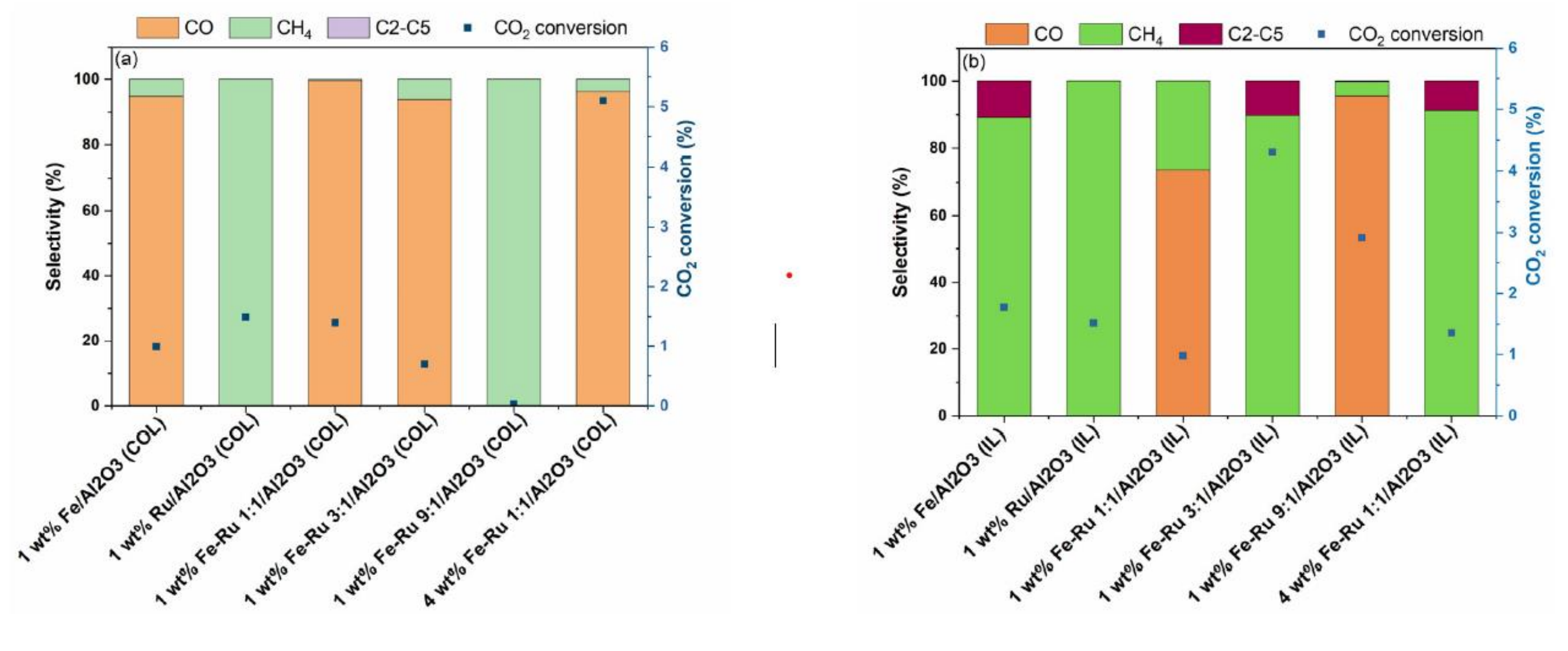


Figure 2b. Comparison of the TPR profiles of 1wt% Fe-Ru/Al_2O_3 (IL) catalysts at three Fe ratios (1:1, 3:1, and 9:1).

3 CATALYTIC ACTIVITY AND CONCLUSIONS

CATALYTIC ACTIVITY



CONCLUSIONS

- Ionic liquids like [BmIm][BF_4] are used to synthetize bifunctional Fe-Ru catalysts for direct CO_2 conversion to LPG.
- SEM-EDX shows uniform Fe and Ru NP distribution on Al_2O_3 support.
- XRF confirms near-theoretical metal loadings with the desired Fe/Ru ratio. The study shows IL synthesis improves catalyst reducibility and Fe-Ru interaction.
- Preliminary catalytic tests at 20 bar and 45 mL/min indicate that variations in reducibility align with catalytic activity differences.
- IL-prepared catalysts show a fivefold increase in CO_2 conversion to LPG hydrocarbons compared to COL-prepared ones.

M. Maddaloni, A. Centeno-Pedrazo, S. Avanzi, N. J. Mazumdar, H. Manyar, N. Artioli, Catalysts, 2023, 13, 1499

REFERENCES

[1]IPCC, Global warming of 1.5°C, 2022
[2]M. D. Porosoff, B. Yan and J. G. Chen, Energy Environ. Sci., 2016, 9, 62–73.
[3]R. W. Dorner, D. R. Hardy, F. W. Williams and H. D. Willauer, Energy Environ. Sci., 2010, 3, 884–890.
[4]A. Aitbekova, E. D. Goodman, L. Wu, A. Boubnov, A. S. Hoffman, A. Genc, H. Cheng, L. Casalena, S. R. Bare and M. Cargnello, Angew. Chemie - Int. Ed., 2019, 58, 17451–17457.

ACKNOWLEDGMENT

Integrated Capture and Conversion of CO2 to Emission Free Fuels, Green Innovation Challenge Fund, under the "Centre for Advanced Sustainable Energy" (CASE) project R3492CCE.