Thermal and Chemical Stability of Ionic Liquids under High-Temperature Conditions

João Fabian[a,*], Murilo L. Alcantara[a], C. Filipe H. B. Sosa[a], João A.P. Coutinho
[a] *CICECO – Aveiro Institute of Materials, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal*
[*] *e-mail: joaofabian@ua.pt*

Ionic liquids (ILs) are increasingly considered as enabling solvents for intensified high-temperature processes, including CO_2 hydrogenation to methanol and gas dehydration. Their tunable physicochemical properties can improve product removal and separation in CO_2 hydrogenation, preferential absorption of methanol and water can shift the reaction equilibrium and promote higher methanol yields[1]. Nevertheless, their applicability ultimately depends on their ability to withstand prolonged thermal and chemical exposure.

IL stability is commonly assessed using the onset decomposition temperature obtained from short, dynamic thermogravimetric analysis (TGA). However, this parameter may not represent long-term operating limits and can overestimate practical stability by 100-300 °C[2]. To address this limitation, we evaluate the temperature associated with 1% mass loss after 10 h as a more representative descriptor of long-term thermal stability. Instead of the 5-7 TGA experiments typically reported for its determination, we investigated a reduced burden methodology with a dynamic TGA and only 1 isothermal TGA.

Chemical stability is also essential because ILs may interact with reaction products, catalysts, and reactor materials during operations at high temperatures. Selected ILs were therefore exposed to conditions representative of CO_2 hydrogenation to methanol at 240 °C, and possible degradation was investigated by ^{1}H and ^{13}C NMR spectroscopy. The combined approach provides practical criteria for assessing IL durability while reducing the effort required to identify suitable candidates for prolonged high-temperature operation.

Acknowledgments

This work was developed within the scope of the project CICECO Aveiro Institute of Materia ls, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MCTES (PIDDAC). This study also received financial support from Illimited project, financed by Horizon Europe agreement n°101192964. Filipe H. B. Sosa acknowledges FCT (CEECIND/07209/2022)

References

(1) Reichert, J.; Maerten, S.; Meltzer, K.; Tremel, A.; Baldauf, M.; Wasserscheid, P.; Albert, J. Sustain. Energy Fuels 2019, **3**, 3399–3405
(2) Cao, Y.; Mu, T. Ind. Eng. Chem. Res. 2014, **53**, 8651–8664.