Cascade Valorization of 5-Hydroxymethylfurfural (HMF) to Monomers and Furanic/Tetrahydrofuranic Diethers Bio-fuels

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The depletion of fossil resources is driving the research towards the renewable ones. Under this perspective, 5-hydroxymethylfurfural (HMF) represents a valuable platform-chemical for the synthesis of monomers and bio-fuels [1]. Thus, the present work proposes, for the first time, a cascade process for the synthesis of diol monomers and furanic/tetrahydrofuranic diethers as novel bio-fuels starting from HMF [2] (Figure 1).

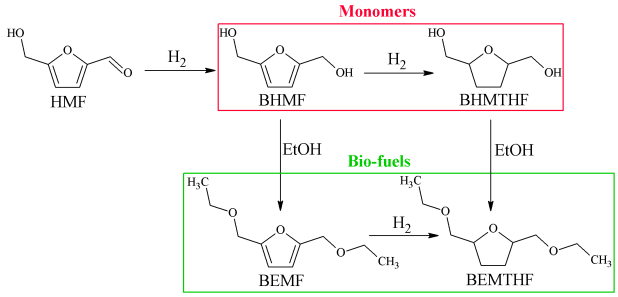

Figure 1. Pathways of the proposed cascade process.

In the first step, the selective hydrogenation of HMF in ethanol to give 2,5-bis(hydroxymethyl)furan (BHMF) or 2,5-bis(hydroxymethyl)tetrahydrofuran (BHMTHF) was carried out by properly tuning the reaction conditions in the presence of 5 wt% Ru/C as catalyst, reaching the highest yields of 80 and 93 mol%, respectively. These diols are important monomers and represent also strategic precursors for two scarcely investigated ethoxylated bio-fuels, 2,5-bis(ethoxymethyl)furan (BEMF) and 2,5-bis(ethoxymethyl)tetrahydrofuran (BEMTHF). Thus, in the second step, the etherification of both pure BHMF and BHMTHF to give BEMF and BEMTHF, respectively, was studied, testing several commercial acid heterogeneous catalysts. The zeolite HZSM-5 (Si/Al = 25) resulted the most promising one thanks to its suitable acidic properties, achieving the highest BEMF yield of 74 mol%. Analogous results were also obtained starting from crude BHMF, recovered from the previous hydrogenation step and directly etherified. On the contrary, BEMTHF was not obtained by the direct etherification of BHMTHF, but a preliminary study showed the possibility of synthesising BEMTHF by the 5 wt% Ru/C catalyzed hydrogenation of BEMF. Finally, the stability of the tested catalysts (5 wt% Ru/C and zeolite HZSM-5) was investigated, showing that both systems maintained the activity almost constant up to five recycle runs, thus resulting recyclable.

References

1. Wan Y., Lee J. M. *ChemSusChem* **2021**, *14*, 1-26.
2. Fulignati S., Antonetti C., Tabanelli T., Cavani, F., Raspolli Galletti, A. M. *ChemSusChem* **2022**, doi:10.1002/cssc.202200241