

SYNTHESIS OF CARBON-BASED BIFUNCTIONAL LEWIS/BRØNSTED ACID CATALYSTS FOR 5-HMF PRODUCTION FROM CELLOBIOSE

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Lignocellulosic biomass has been recognized as a promising renewable resource for the production of a number of key commodity chemicals. Among the possible products that can be obtained by upgrading its cellulose component, 5-hydroxymethylfurfural (5-HMF) is a high added-value platform chemical that can be valorized. Transforming cellulose into 5-HMF requires three steps involving hydrolysis of the biomass, isomerization of the attained glucose into fructose, and the subsequent dehydration of the latter into 5-HMF [1] (**Figure 1**). Therefore, there is a strong interest in developing bifunctional catalysts presenting both Brønsted and Lewis acid sites for favoring this multi-step transformation in one pot. In addition, the use of a carbon solid support can provide superior mechanical and chemical resistance to the water and O-rich media provided by such a feedstock, along with tunable textural and surface properties.

In the present work, mesoporous aluminosilicate patches [2-3] have been grafted on the surface of a carbon support (activated carbon powder, fraction < 50µm) together with benzyl sulfonic moieties [4] to provide both Lewis and Brønsted acid sites, respectively, to the same solid. To study the elemental composition and microstructural features achieved, SEM/EDX, TEM (**Figure 1**), and XPS analyses have been performed. Nitrogen physisorption was used to confirm the mesoporous nature of the catalysts, while Boehm titration and ^{31}P MAS NMR with PMe_3 probe were applied to investigate their acidity and confirm the presence of both Brønsted and Lewis sites in the final material. The activity of the synthesized bifunctional catalysts and that of their corresponding monofunctional counterparts (sulfonated carbon and aluminosilicate patched carbons) was compared for the upgrading of cellobiose to 5-HMF. A proximity effect was found when the two acidic sites are combined onto the same substrate, facilitating the overall conversion of the sugars involved. A maximal yield of 37% of 5-HMF was attained after 23 h with catalyst I4@BATEOS/ SO_3H in a THF:mQ water system at 423 K. No significant traces of side products were observed after 23 hours, indicating the high selectivity of the catalyst for the targeted transformations.

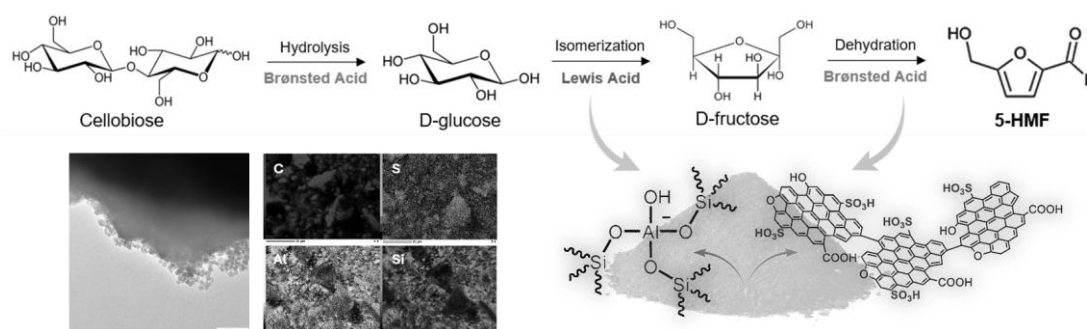


Figure 1: Synthesis of 5-hydroxymethylfurfural (5-HMF) from cellobiose mediated by Brønsted (benzyl sulfonic moieties) and Lewis (aluminosilicate patches) acid sites co-located at the surface of an activated carbon support. On the left side, a TEM image of the obtained oxide patches and corresponding SEM-EDX maps. On the right, schematic representation of the final material.

References:

- [1] Y. Yao, S. Chen, M. Zhang, *Front. Chem.* 10 (2022), 880603
- [2] T. Haynes et al., *Appl. Cat. B* 241 (2019), 196 – 204
- [3] T. Haynes et al., *ChemCatChem* 11 (2019), 4054 – 4063
- [4] S. Carlier, S. Hermans, *Front. Chem.* 8 (2020), 347