Carbon-based bifunctional Lewis/Brønsted acid catalysts for 5-HMF production from cellobiose

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As a renewable resource, lignocellulosic biomass holds significant potential for producing important commodity chemicals like 5-hydroxymethylfurfural (5-HMF), which can be obtained from its cellulosic fraction through a three-step Brønsted and Lewis acid catalyzed reaction [1]. Due to the highly oxygenated nature of biomass, an activated carbon powder (AC, fraction < 50µm) has been selected as support for this study, owing to its excellent mechanical and chemical resilience in such environment, combined with tunable textural and surface properties.

Bifunctional carbon-based acid catalysts were successfully synthesized by co-locating mesoporous aluminosilicate patches [2-3] and benzyl sulfonic moieties on the same substrate's surface, conferring both Lewis and Brønsted acidity, respectively (**Fig.1** and **Tab.1**). Patches were necessary to preserve some bare carbon surface for sulfonic acid grafting, performed via a diazonium coupling methodology [4] to ensure robust anchoring. The bifunctional catalysts obtained and their monofunctional equivalents (sulfonated carbon and aluminosilicate patched carbons) were fully characterized and compared in terms of catalytic activity for the upgrading of cellobiose to 5-hydroxymethylfurfural. Bifunctional catalysts I0@BATEOS/SO_3H (higher Al/Si content) and I4@BATEOS/SO_3H (lower Al/Si content) were found to be more active than their monofunctional analogues, proving that a synergy was brought about by the proximity of the two acid sites onto the same substrate. A maximal 37% 5-HMF yield was obtained out of a 96% cellobiose conversion after 23h with catalyst I4@BATEOS/SO_3H in a THF:mQ water solvent mixture at 423 K. Negligible traces of sugary side-products have been found, proving the high selectivity of the catalyst for the designed process.

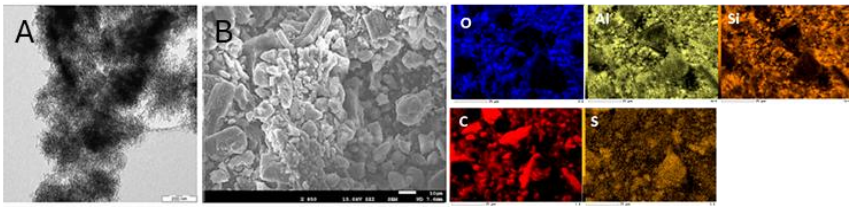

Fig.1: TEM (A), SEM images (B) and EDX maps for catalyst I4@BATEOS/SO_3H

Tab.1: Textural properties and total acidity measured via Bohem back titration of the main materials; BET specific surface area (S_{BET}) and pore volume (V_p) determined via the Barrett-Joyner-Halenda model applied on nitrogen physisorption data.

Entry	S_{BET} [m^2/g]	V_p [cm^3/g]	Pore size [Å]	Total acidity [mmol/g]
Activated Carbon	912.6	0.34	17.6	0.04
AC@SO_3H	123.7	0.17	31.7	1.33
I0@BATEOS/SO_3H	187.1	0.14	26.6	1.66
I4@BATEOS/SO_3H	88.6	0.12	45.8	1.25

References

[1] Yao, Y.; Chen, S.; Zhang, M. *Front. Chem.* **2022**, *10*, Article 880603
[2] Haynes, T.; D'hondt, T.; Morritt, A. L.; et al. *ChemCatChem* **2019**, *11*, 4054 – 4063
[3] Haynes, T.; Ersen, O.; Dubois, V.; et al. *Appl. Cat. B* **2019**, *241*, 196 – 204
[4] Carlier, S., Hermans, S. *Front. Chem.* **2020**, *8*, Article 347