Development of bifunctional carbon-based acid catalysts for the conversion of cellobiose into 5-hydroxymethylfurfural (5-HMF)

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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 must be recovered and valorised. The designed acid-catalysed process consists of three steps involving hydrolysis of the biomass, isomerization of the attained glucose into fructose, and the subsequent dehydration of the latter to 5-HMF [1]. Hence, there is strong interest in developing carbon-based catalysts presenting the perfect balance between Brønsted and Lewis acid moieties for favouring this transformation. A carbon solid support possesses all the advantages of a heterogeneous system along with good mechanical and chemical resistance in water and in the O-rich media provided by the biomass, ease of functionalization, and availability in multiple different forms offering controlled and tuneable textural features.

In the present work, aluminosilicate islands have been grown on the selected carbon substrate (activated carbon powder SX+ from Norit, fraction < 50µm) as Brønsted/Lewis acidity providers. The partial coverage of the substrate by the mesoporous metal-oxide layer is achieved by using bis(sec-butoxy)aluminoxy-triethoxysilane [$(sec\text{-}BuO)_2AlOSi(OEt)_3$] as a single source molecular precursor for both aluminium and silicon. An aminosilane (APTES) is also employed to covalently bind the aluminosilicate to the carbonaceous support (Fig.1). Additional Brønsted acid sites (sulfonic groups) have been grafted onto the available carbon free surface in a second step by means of a diazonium coupling method [4].

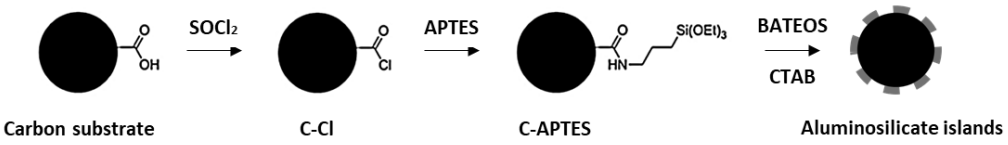

***Figure 1**: Synthesis of aluminosilicate islands on a carbonaceous substrate [3]*

Characterization and catalytic testing play a fundamental role in unveiling the structure-activity relationships. Therefore, SEM/EDX, TEM, and XPS analyses have been performed to assess the elemental composition of the attained catalysts, together with providing an insight into their microstructural features. To study porosity and acidity, nitrogen physisorption and Boehm titrations have been carried out, respectively.
As a final step, some preliminary catalytic tests have been performed at 150 °C under 4.7 bar of N_2 autogenic pressure for 4h starting from cellobiose as a model for cellulose; a biphasic environment THF:water (mQ) is set as reaction media.
The synthesized systems have been compared in terms of cellobiose conversion and yield in 5-HMF to pinpoint the impact of the catalysts' synthesis parameters on the targeted reaction.
With the successful synthesis of active bi-functional catalysts, future studies will focus on assessing their stability and recyclability over time.

References

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