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Tuning the Acid Strength and Surface Polarity of Silica-Supported Sulfonic Acid Catalysts

AUTHORS

Antony FERNANDES / UCLOUVAIN, INSTITUTE OF CONDENSED MATTER AND NANOSCIENCES
BOLTZMANN A.241, PLACE CROIX DU SUD, 1 BOX L7.04.02, LOUVAIN-LA-NEUVE

PURPOSE OF THE ABSTRACT

Solid acid catalysts are central in our chemical industry and are becoming critical for the conversion of bioresources. However, there is still a need to design catalysts with improved acid strength and tunable surface polarity to improve or enable chemical transformations in a more sustainable initiative. Noteworthy, the performances and reusability of solid acid catalysts can depend strongly on the surface polarity, as the later affects directly the transport and adsorption/desorption of reactants and products. Hence, it might be necessary in some instances to counterbalance the intrinsic hydrophilicity of acid sites to achieve catalytic systems that are not mainly diffusion-controlled. This design principle is especially relevant for reactions involving less polar reactants or for reactions wherein water, as a solvent, reactant or by-product, is involved; water that causes drop of the acid strength and partial deactivation of the catalytic sites. Modular methods allowing to fine tune the acid strength as well as the local environment of the active centers are thus requested.

Here, we present the development of a robust and flexible strategy for the preparation of silica-supported sulfonic acid catalysts that mirrors more conventional approaches based on mercaptosilanes (Figure 1). Precisely, we extended our recent strategy centered on the copper-catalyzed azide-alkyne cycloaddition (CuAAC) chemistry[1-3] to the covalent grafting of organosulfonic acids on mesoporous silica. We demonstrate that the triazole link, resulting from the quantitative grafting of propargylsulfonates on azide-functionalized mesoporous silica, provides a unique handle to modulate the acid strength of the catalyst. Converting the triazole into an electron-withdrawing triazolium results in significant increase of the acid strength and activity of the catalytst. Moreover, we show that the later triazole can also serve as an anchoring point for both the sulfonic acids and secondary groups, resulting in paired bifunctional catalytic systems. As an example, we show that pairing sulfonic acid and hydrophobic groups allows to significantly improve the performances of the solid catalysts; performances that are severely reduced with monofunctional acid catalysts or when pairing the sulfonic acid with hydrophilic chains.

These results illustrate that our method provides significant opportunities for the rational design, precision preparation and modular tuning of supported acid catalysts. It uncovers, therefore, a new entryway to supported catalysts with finely adjustable properties that lies well beyond the molecular design of the active center itself.

FIGURES

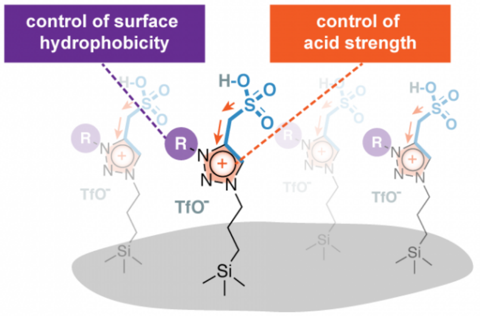

FIGURE 1

Figure 1.

Silica-supported sulfonic acid catalysts with tunable acid strength and surface polarity

FIGURE 2

KEYWORDS

supported catalysis | multifunctional catalysts

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