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Green and Scalable Synthesis of UiO-66-SO3H Metal-Organic Framework and its Catalytic Activity in Dehydration of Fructose

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PURPOSE OF THE ABSTRACT

Metal-Organic Frameworks (MOFs) are hybrid crystalline microporous solids. Their hybrid nature comprising both inorganic metal sites (ions, clusters) and organic ligands allows for unique 1-, 2- or 3D structures. With more than 90 000 synthesized structures since their discovery, MOFs have taken leading positions in materials science with numerous applications in gas storage, sensing, energy storage, catalysis, water purification and others [1,2]. UiO-66 (Universitetet i Oslo) is one of the most famous MOFs nowadays. Built of Zr-oxoclusters and terephthalate linkers, UiO-66 exhibits a continuous 3D structure with pronounced textural properties such as surface areas surpassing 1000 m2 g-1 and cages with diameters of 7.5 and 12 Å [3]. Moreover, free metal sites on the Zr-oxoclusters provide Lewis acid sites which together with the MOF's chemical and thermal stabilities enable applications in various media and elevated temperatures (< 450 °C). Besides, by employing functionalized linkers (sulfo-, aminoterephtalates etc.) it is possible to insert functional groups into the UiO-66 framework to eventually form UiO-66-X (where X is -SO3H, -COOH, -NH2 or others). This opens up the possibility to apply functionalized UiO-66-X in a wide variety of chemical processes requiring either Brønsted acid or base sites.
Nevertheless, one of the challenges concerning MOFs production and application on industrial scale is upscaling and shaping [4]. Indeed, oftentimes MOFs synthesis implies using hazardous and toxic solvents (such as DMF: N,N-dimethylformamide) which hinders their further implementation on large industrial scale production and application. Therefore, this work is an attempt to overcome these issues and provide an example of a green, scalable synthesis of a UiO-66 based MOF with its further application in the conversion of a biomass derived molecule. The strategy of this work is built around UiO-66-SO3H and includes several steps (Fig. 1): 1) small scale synthesis in H2O; 2) synthesis upscaling in a 3-L reactor; 3) MOF shaping into extrudates; 4) application in catalytic dehydration of fructose into 5-hydroxymethylfurfural (5-HMF). The latter is intended to probe its newly formed Brønsted acid sites provided by -SO3H groups. Once the reaction conditions were optimized, UiO-66-SO3H showed superior 70 % fructose conversion and 40 % 5-HMF yield under mild conditions (60 °C) and low fructose-to-catalyst weight ratio (11:1). The identical test over the classical UiO-66 and blank (no catalyst) test demonstrated no fructose conversion which allows to confirm the positive effect of -SO3H groups as well as to eliminate the solvent effect (dimethylsulfoxide, DMSO). The presented work then includes the upscaling and shaping applied on UiO-66-SO3H powder to highlight the effect of extrusion on the structural, textural and catalytic properties of the parent MOF.

FIGURES

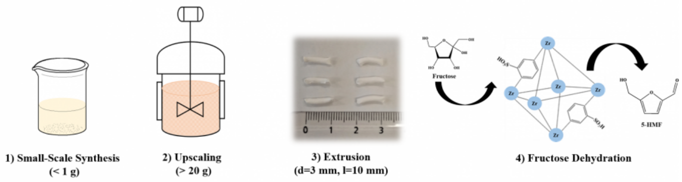

FIGURE 1

Fig. 1

Schematic representation of the steps performed in this work

FIGURE 2

KEYWORDS

Metal-Organic Framework | Upscaling | Shaping | Dehydration

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