



## Efficient catalytic conversion of carbohydrates into 5-ethoxymethylfurfural over MIL-101-based sulfated porous coordination polymers<sup>☆</sup>

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### ABSTRACT

In this work, a series of MIL-101-SO<sub>3</sub>H(x) polymeric materials were prepared and further used for the first time as efficient heterogeneous catalysts for the conversion of fructose-based carbohydrates into 5-ethoxymethylfurfural (EMF) in a renewable mixed solvent system consisting of ethanol and tetrahydrofuran (THF). The influence of -SO<sub>3</sub>H content on the acidity as well as on the catalytic activity of the porous coordination polymers in EMF production was also studied. High EMF yields of 67.7% and 54.2% could be successively obtained from fructose and inulin in the presence of MIL-101-SO<sub>3</sub>H (100) at 130 °C for 15 h. The catalyst could be reused for five times without significant loss of its activity and the recovery process was facile and simple. This work provides a new platform by application of porous coordination polymers (PCPs) for the production of the potential liquid fuel molecule EMF from biomass in a sustainable solvent system.

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### 1. Introduction

With the gradual depletion of fossil fuels and degradation of the environmental deterioration over the last decades [1], the exploration of renewable resources for the production of biofuels and chemicals was regarded as one of the major challenges. Increasing attention has been laid on efficient conversion of biomass-derived carbohydrates to useful platform molecules in green and sustainable chemistry [2]. Among various biomass-derived chemicals, furanic compounds which can be used as valuable intermediates for fine chemicals, pharmaceuticals and furan-based polymers have caused great concern [3,4].

5-Ethoxymethylfurfural (EMF), an etherification product of HMF, has already been developed as a potential diesel fuel blending agent [5]. EMF has a high energy density of 8.7 kWh/L, which is comparable to the standard gasoline (8.8 kWh/L)

and diesel (9.7 kWh/L), and is 29% greater than that of bio-ethanol (6.1 kWh/L) [6]. Generally, EMF can be synthesized from 5-hydroxymethylfurfural (HMF) or 5-chloromethylfurfural (CMF) with high yields [7,8] while the large-scale production of EMF from these furanic compounds is still limited due to the high cost of catalysts and the substrates involved. Recently, much effort of heterogeneous catalysts has been taken to synthesize EMF from fructose. When sulfonated solid materials like silica [9] and magnetic Fe<sub>3</sub>O<sub>4</sub>@C [10] were used as catalysts, a high EMF yield of 63.1% and 67.8% could be achieved. The catalysts by immobilizing soluble acids phosphotungstic acid (HPW) onto supports such as silica-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles [11], K-10 clay [12], and MCM-41 [13] showed EMF yields of 54.8%, 61.5%, and 42.9%, respectively. Results indicated that Brønsted acid catalysts were efficient for the conversion of fructose to EMF. Given the relatively high price of fructose, inulin as a polyfructan obtained in large quantities from plants of the *Compositae* family [14] is considered as an ideal source for production of D-fructose-derived chemicals. Hence, the catalytic sequential hydrolysis–dehydration–etherification of inulin into EMF with more efficient, easily available Brønsted acid active sites and adjustable pore structure is still in urgent demand.

Porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) are a new class of crystalline hybrid materials assembled of metal ions or metal-containing secondary building

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units (SBUs) and bi- or multimodal organic linkers [15,16]. The unique advantage of PCPs is highly designable frameworks by tailoring the organic linker, which provides diversity pore surfaces and pore structures. Among more than 20,000 well-known MOFs, several unique features such as a rigid zeolite crystal structure extremely large surface area and pore size, numerous unsaturated metal cation sites (CUS), and high hydrothermal and chemical stability [17,18] make MIL-101 a unique candidate for catalysis [19]. Phosphotungstic acid (PTA)/MIL-101(Cr) was one of initial examples of application of PCPs for dehydration of carbohydrates to produce HMF with a yield of 63% in DMSO for 30 min at 130 °C [20]. Metal-organic framework MIL-53(Al) without any functionalization was also employed as an efficient heterogeneous catalyst for synthesis of HMF from carboxymethyl cellulose (CMC) in water, and a moderate HMF yield of 40.3% along with a total reducing sugar (TRS) yield of 54.2% could be obtained at 200 °C for 4 h [21]. A sulfonic acid functionalized MIL-101(Cr) [MIL-101(Cr)-SO<sub>3</sub>H] was synthesized but almost inert for cellulose hydrolysis, giving only 5.3% yield of total mono- and disaccharides at 120 °C for 3 h in water [22]. Very recently, MOF-SO<sub>3</sub>H materials prepared by postsynthetic modification (PSM) were used to catalyze fructose-to-HMF transformation in DMSO, achieving 90% HMF yield for a complete fructose conversion at 120 °C in 60 min [23]. These results indicated that the presence of SO<sub>3</sub>H groups in MOFs was strongly enough to promote the dehydration reactions. However, the separation of the product from DMSO requires significant energy input to evaporate the volatile solvent, as compared with biomass-based solvents (e.g., THF) with low boiling points.

Despite the low solubility of sugars in alcohols, the intact structure of MOFs is likely to be kept in this type of solvents other than water under relatively moderate reaction conditions. Given this, the further extend of catalytic applications of MIL-101 for biomass valorization and transformation of carbohydrates to EMF in environmental friendly solvent system should be inquired. Herein, a series of MIL-101-SO<sub>3</sub>H(*x*) materials were demonstrated to have great potential to act as efficient heterogeneous catalysts for conversion of fructose-based carbohydrates into EMF in a renewable mixed solvent of ethanol-THF, both of which were derived from biomass. Meanwhile, the influence of -SO<sub>3</sub>H content on the acidity by varying the ratio of terephthalic acid and sulfonated terephthalic acid in the starting solution, and the effect of acidity on the catalytic activity were also investigated.

## 2. Experimental

### 2.1. Materials

2-Sulfoterephthalic acid monosodium salt (>98%) purchased from J&K Chemical Ltd; EMF (97%) was obtained from Sigma-Aldrich, and protonated Nafion NR50 was purchased from Alfa Aesar (Tianjin, China). Terephthalic acid (99%), Amberlyst-15, fructose, glucose, sucrose, cellobiose, inulin, and HMF in analytical grade were purchased from Shanghai Aladdin Industrial Inc; other chemicals (AR grade) were used without further purification. Solvents were dried according to standard methods and stored in the presence of molecular sieves. Deionized water was obtained from AXL-C1820 Water ultrapure water purification system.

### 2.2. Preparation of MIL-101, a series of sulfonic acid functionalized MIL-101(MIL-101-SO<sub>3</sub>H(*x*)) and other sulfated solid acid catalysts

MIL-101 was synthesized using a reported method [17]. The preparation of MIL-101-SO<sub>3</sub>H by hydrothermal method was carried out, according to a recent literature [22] with slight modifications. In a general procedure, 2-sulfoterephthalic acid monosodium salt (2-NaSO<sub>3</sub>-H<sub>2</sub>BDC) (3.35 g, 12.5 mmol), CrO<sub>3</sub> (1.25 g, 12.5 mmol),

and concentrated hydrochloric acid (12 M, 0.91 g) were dissolved into 50 mL of deionized water and stirred for a few minutes at room temperature. The resulting mixture was then transferred to a Teflon-lined stainless steel autoclave maintained in an oven at 180 °C for 6 d. The produced solid was filtered and washed with deionized water and then with methanol three times. The resulting sulfonic acid-functionalized MIL-101 was denoted as MIL-101-SO<sub>3</sub>H(100).

For preparation of MIL-101-SO<sub>3</sub>H(*x*) (*x*% denotes the ratio of 2-NaSO<sub>3</sub>-H<sub>2</sub>BDC to H<sub>2</sub>BDC in the synthetic solution, *x* = 25, 50, 75, and 90) with varying amounts of sulfonic-acid groups, a mixture of 2-NaSO<sub>3</sub>-H<sub>2</sub>BDC and terephthalic acid (H<sub>2</sub>BDC) with various molar ratios of 1:3, 1:1, 3:1, and 1:9 was employed in the starting solution, and the resulting sample was denoted as MIL-101-SO<sub>3</sub>H(90), MIL-101-SO<sub>3</sub>H(75), MIL-101-SO<sub>3</sub>H(50), and MIL-101-SO<sub>3</sub>H(25), respectively. For comparison, SO<sub>4</sub><sup>2-</sup>/Nb<sub>2</sub>O<sub>5</sub> and SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> catalysts were also prepared by following previously described methods [24–26].

### 2.3. Catalysts characterization

The crystalline structures were analyzed by X-ray diffraction (XRD) with a Shimadzu XRD-6000 diffractometer using Cu K $\alpha$  radiation ( $\lambda$  = 0.1541 nm) in a scanning range of 2–10 °C at 0.5°/min. The textural properties of the prepared samples were measured by N<sub>2</sub> adsorption at –196 °C in a Micromeritics ASAP 2020 instrument. The sample was outgassed in vacuum at 150 °C for 10 h prior to the adsorption measurement. FT-IR spectra were recorded on a Nicolet 360 FT-IR instrument (KBr disks). The amount of sulfonic acid groups of MIL-101-SO<sub>3</sub>H(*x*) was determined by acid-base titration using NaCl solution as an ion-exchange agent. In a typical procedure, 0.5 g of MIL-101-SO<sub>3</sub>H(*x*) was suspended in 20 g of aqueous NaCl saturated solution. The resulting suspension was stirred at room temperature for at least 24 h until the equilibrium reached, followed by filtration and washing with 30 mL of deionized water. Finally, the filtrate was titrated with 0.1 M NaOH solution. For comparison, elemental analysis by Vario EL III was used to determine the contents of sulfur in the MIL-101-SO<sub>3</sub>H(*x*) catalysts. The thermal stability of MIL-101-SO<sub>3</sub>H(*x*) was measured by thermogravimetry (TG), carried out with a Beifen PCT-IA instrument in a nitrogen atmosphere (heating rate: 5 °C/min). The morphology of the catalysts was investigated using a field-emission scanning electron microscopy (FE-SEM) Zeiss SUPRA 55 with an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) images were recorded with Philips Tecnai 20 and JEOL JEM-2010 HR-TEM. The accelerating voltage was 200 kV in each case.

### 2.4. General procedure for catalytic conversion of fructose into EMF

In a typical procedure, fructose (180 mg, 1 mmol), the MIL-101-SO<sub>3</sub>H(*x*) catalyst (100 mg), and ethanol (5 mL) with co-solvent THF (4 mL) were added into a 25 mL stainless steel vessel with a Teflon lining and sealed by a screw cap. The reactor was placed into preheated oil maintained at 130 °C under autogeneous pressure for 15 h with a magnetic stirrer. Zero time was recorded when the reactor was immersed into the preheated oil bath. After the desired reaction time, the reactor was quickly removed from the oil bath and quenched the reaction by tap-water. Samples were withdrawn, diluted with ethanol, and centrifuged at 12,000 rpm for 5 min. The clear liquid was filtered with a 0.45  $\mu$ m syringe filter prior to analysis by high-performance liquid chromatography (HPLC) system.

### 2.5. Product analysis

Quantitative analysis of HMF and EMF was implemented by an Agilent 1100 HPLC equipped with a UV detector. Samples were

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