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Exceptionally Efficient and Recyclable Heterogeneous Metal-Organic Framework Catalyst for Glucose Isomerization in Water

Ryan Oozeerally,[a] David L. Burnett,[b] Thomas W. Chamberlain,[b] Richard I. Walton,*[b] and Volkan Degirmenci*[a]

Abstract: Heterogeneous catalysts are desired for the conversion of glucose, the most abundant sugar in renewable biomass, but presently their synthesis requires highly toxic chemicals with long synthesis times. We report the conversion of glucose to fructose and 5-hydroxymethyl furfural on a heterogeneous catalyst that is stable and selective and operates in most environmentally benign solvent, water. We used a bi-functional solid with Lewis and Brønsted acid sites by partially replacing the organic linker of the zirconium organic framework UiO-66 with 2-mono-sulfo-benzene-1,4-dicarboxylate. This catalyst shows high product selectivity (90 %) of 5-hydroxymethylfurfural and fructose at 140°C in water after 3 h reaction. It is recyclable and shows only minor loss of activity after a 3rd recycle, offering a realistic solution for the bottleneck reaction of glucose isomerization for scale up and industrial application of biomass utilization.

Sustainable production of chemicals requires the utilization of renewable resources, one of the most promising of which is lignocellulosic biomass.[1-2] Biomass derived sugars (e.g., glucose or fructose) can be converted into platform molecules, e.g. 5-hydroxymethyl furfural (HMF), which can be further processed into monomers, fuel additives, paints and a variety of fine chemicals envisaged in a future biorefinery[3-4]. Although fructose can be converted into HMF easily[5], glucose is the main building block of lignocellulosic biomass and its conversion remains challenging.[4] The best performing heterogeneous catalyst for this conversion is tin-incorporated beta zeolite (Sn-beta) with Sn^{4+} occupying a fraction of tetrahedral sites in the zeolite framework.[6-8] Sn-beta can effect the isomerization of glucose to fructose in water with high selectivity (> 50%).[7] However, Sn-beta requires long crystallization times, up to 40 days, which is industrially unviable, at high temperatures, 140°C, and, moreover, requires the use of hydrofluoric acid, an acute poison and extremely corrosive.[7] In this work, we present a recyclable catalyst for glucose isomerization. It is based on modified UiO-66 (Figure 1a),[9] a thermally and hydrothermally robust metal-organic framework (MOF), which we show matches the conversion and product selectivity of Sn-beta.

The advantage of using MOFs as heterogeneous catalysts is the potential for tuning the solids' properties by inclusion of desired functional ligands[10], such as acid sites,[11] and at the same time via simple synthesis protocols; in this case without highly toxic and corrosive HF,[12] in less than 24 h at 120°C.

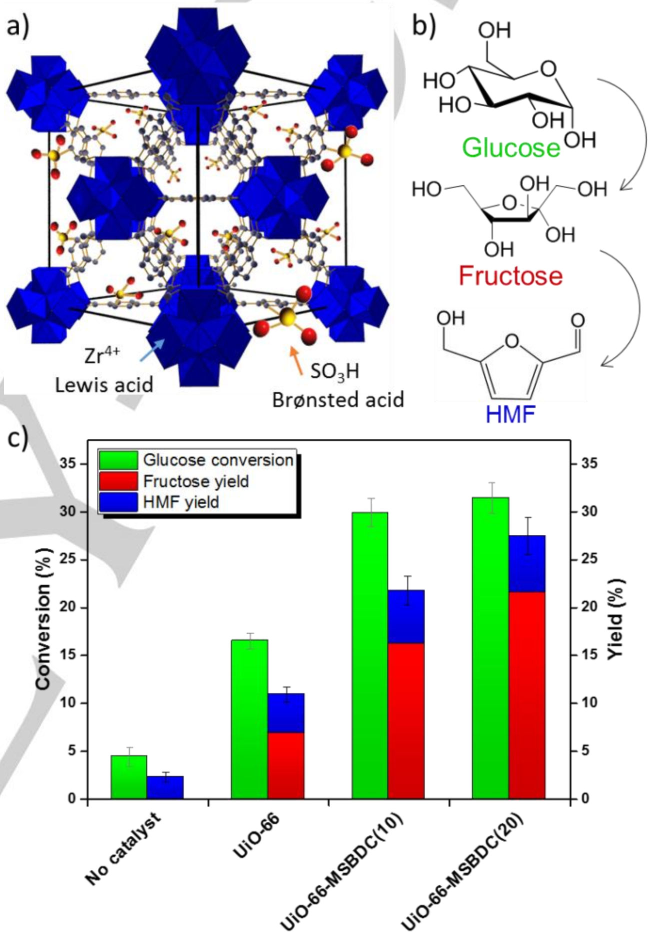

Figure 1. a) Schematic representation of UiO-66 framework. b) Glucose conversion to HMF through isomerization into fructose; c) Isomerization of glucose in water on metal organic framework catalysts; UiO-66, UiO-66-MSBDC(10) and UiO-66-MSBDC(20). Reaction conditions: 140 °C, 3 hours, stock solution of 10 wt. % glucose in deionized water.

The challenge in the HMF production from glucose is to achieve high product selectivity. The reaction proceeds through isomerization of glucose to fructose (Figure 1b)[13] which is the limiting step to achieve high selectivity. It is proposed in the literature that the reaction is catalysed by Lewis acids[13], which enable a hydride shift between carbon atoms of glucose[14], at the same time, proximal silanol groups or Brønsted acid sites form a hydrogen-bonding network, facilitating the proton mobility[15]. UiO-66 is a zirconium-based MOF with benzene-1,4-dicarboxylate (BDC) linkers, showing high stability in air up to 500°C as well as hydrothermal inertness[9]. Defects in the form of coordinatively unsaturated Zr^{4+} sites provide Lewis acidity.[16] We find that UiO-66 itself is active in glucose conversion (Figure

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1c) showing 16 % conversion accompanied with 10 % product yield at 140°C in 3 h. However, it lacks Brønsted acid sites. Therefore, we used a catalyst synthesized by partially replacing the BDC linker with 2-mono sulfonated benzene-1,4-dicarboxylic acid (MSBDC)[17-18] which shows 31 % glucose conversion under same reaction conditions with 28 % product yield (Figure 1c). This corresponds to an exceptional product selectivity of around 90 %, which is similar to previously reported Sn-beta zeolite.[7]

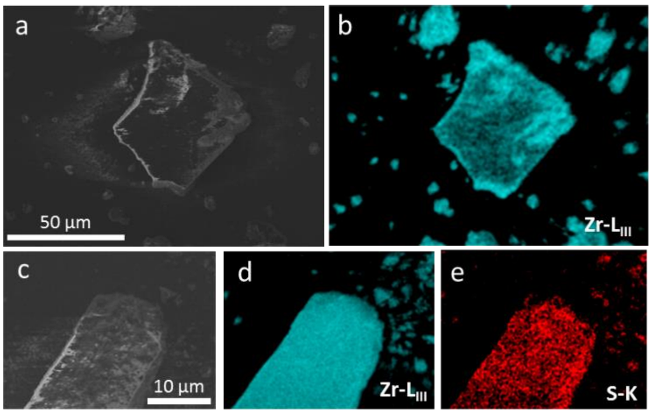

Figure 2. SEM Image (a) and zirconium EDX mapping of UiO-66. SEM Image (c), zirconium (d) and sulfur (e) EDX mapping of UiO-66-MSBDC(20).

The ratio between BDC and MSBDC linkers is critical for the successful synthesis of a stable functionalized UiO-66 material. Higher ratios of MSBDC within the framework have already been shown to decrease the stability UiO-66.[9, 18] Indeed, we find that if only MSBDC is used as the ligand then the material subsequently collapses on hydrothermal treatment (Supporting Information, Figure S1). As such, materials containing 10 and 20 percent functionalized linker were synthesized (UiO-66-MSBDC(y); where y represents the mol. % of MSBDC linker in total linker content). SEM images (Figure 2a, c) show the particle morphology of UiO-66 and UiO-66-MSBDC(20). Zirconium EDX mapping (Figure 2b, d) demonstrates the uniform distribution of zirconium atoms in both MOF structures, while, sulfur EDX mapping of the UiO-66-BDC(20) catalyst (Figure 2e) indicates a similar distribution of modified linker across the MOF crystal. Although EDXA mapping does not give information on the 3-dimensional distribution, it clearly implies the uniform distribution of Brønsted acid sites with some evidence for enrichment at the crystal surface UiO-66-MSBDC(20) catalyst (See SI Figure S2 for all catalysts). Further, EDX analysis of the MSBDC containing materials reveals an absence of sodium, supported by bulk ICP-OES analysis, consistent with the displacement of sodium ions during synthesis to yield Brønsted acidic SO_3H sites.

The incorporation of sulfonic acid groups was also confirmed through FT-IR spectroscopy. New peaks appear in the UiO-66-MSBDC catalysts at 620, 1078, 1180 and 1223 cm^{-1} and their intensity increases with the increasing linker content (See SI Figure S3). These bands are attributed to the characteristic asymmetric bending and symmetric and asymmetric stretching of S=O double bonds and S-O bonds.[19-20] Elemental analyses of fresh catalysts also show S:Zr ratios close to the expected values (See SI Table S1 and S2). Thermogravimetric analysis (TGA) shows an extensive loss in mass at around 510°C for both the standard and functionalized UiO-66 materials (See SI Figure S4). This is consistent with the reported decomposition temperature of 540°C for UiO-66 and approximately 500°C for sulfonic UiO-66 materials reported in literature.[9, 18] Mass loss indicates an MSBDC linker content of 14.6 % and 24.7 % for UiO-66-MSBDC(10) and UiO-66-MSBDC(20), respectively, close to the expected values. As a result, the ratio of the zirconium:linker in UiO-66, UiO-66-MSBDC(10) and UiO-66-MSBDC(20) were found as 5.51, 5.11 and 5.63 respectively and thus coordinatively unsaturated Zr^{4+} sites are present (See SI Table S3 and S4).

Powder X-ray diffraction (PXRD) analysis of the catalysts shows the formation of crystalline MOF structures (Figure 3a). Indeed, the addition of the MSBDC did not alter the average structure of UiO-66. The lattice parameter of the fresh UiO-66 was determined as 20.7516(2) Å (See SI Figure S5). This value compares well with the reported literate value of 20.7551(5) Å,[9] while the lattice parameter of UiO-66-MSBDC(20) was determined as 20.7431(13) Å (Figure 3a) and a similar result was obtained for UiO-66-MSBDC(10) (See SI Figure S5).

The significant increase in fructose yields, combined with marginal increases in HMF yields, suggests that the modification of UiO-66 with MSBDC could affect the Lewis acidity in two ways. First, more defective materials are formed; this is supported by the increase in the mesopore volume of the UiO-66-MSBDC catalysts (See SI Table S5 and Figure S6). Second, the Lewis acidity of Zr^{4+} is known to be enhanced significantly by the presence of a nearby electron-withdrawing group that has been extensively studied in sulfated zirconia catalysts.[21] This effect has recently been reported in MOFs in the presence of electron withdrawing fictional groups such as $-NO_2$ on the organic linker;[22] indeed, we find that $-NO_2$ modified UiO-66 shows improved conversion over the parent material (Figure S8) and so it is conceivable that the sulfonyl acid groups have a similar effect. Clearly, further work is needed to understand fully the interplay of the acid functionalities.

The recyclability of the catalysts is crucial for scale up and industrial application: we studied this by recovering the solid catalysts using a centrifuge and washing with water after each reaction cycle. It was observed that full recovery of the catalysts was not possible due to the presence of small catalyst particles that remained dispersed in the reaction medium. These nanocrystalline materials have intrinsically higher activity (Figure S8). However, once the small particles are filtered out after the first run, all the catalyst is recoverable in the consecutive reaction cycles (See SI Table S6). Therefore, although a decrease in glucose conversion was observed after the first run, no loss of activity was observed in the following 3 recycles (Figure 3b), particularly for the UiO-66-MSBDC(20) catalyst (See SI Table S9 for product yields). The PXRD pattern of the UiO-66-MSBDC(20), which was recovered after four runs shows that the integrity of the MOF lattice is maintained (Figure 3a). Zirconium and sulfur EDX mapping of the catalysts after four reaction cycles further confirmed the integrity of the recycled catalysts (See SI Figure S2). The recycling of UiO-66 and UiO-

66-MSBDC(10) catalysts show minor loss of activity after the 4th run. This loss in activity could be in part due to the formation of undesired side products, such as humins. These are poorly characterized oligomeric species, which are known to be the main side product of this reaction[3]. These insoluble products can accumulate on the catalyst surface and block the active sites. Indeed, the recovered catalyst mass in recycle tests increased due to the collection of inseparable side products (See SI Table S3), would explain the lower sulfur counts in EDX analysis of the recycled catalyst as compared to fresh catalysts.

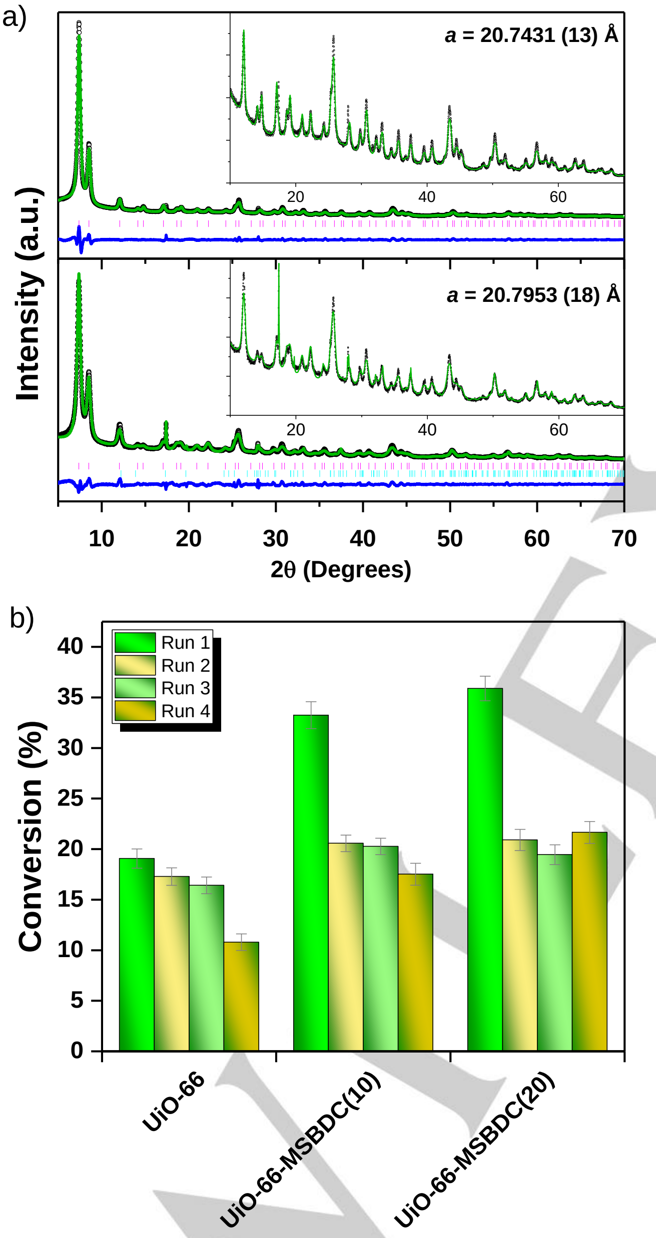

Figure 3. a) PXRD patterns of the UiO-66-MSBDC(20) as fresh catalyst (above) and after the 4th run (below). Insets show the 2 theta region between 10 and 70 degrees. The green lines are the fitted profile, black dots are observed data and the blue line is the difference in the two patterns. The ticks represent positions of allowed Bragg peaks: pink for UiO-66 and pale blue,1,4-benzenedicarboxylic acid. b) Glucose conversion after recycle tests.

It is important to note, however, that elemental analysis of the reaction solution after first reaction cycle (3 h reaction at 140°C) showed only trace amounts of sulfur and zirconium present showing the stability of the catalyst with negligible leaching during the reaction (See SI Table S4). Finally, the performance of the UiO-66 materials were compared to Sn-beta. In the literature, Sn-beta is used as a glucose isomerization catalyst with a Sn to glucose ratio of 1:50 and catalyst weight of Sn-beta far exceeds the amount of MOF catalyst used in this study under similar reaction conditions, where Sn-beta shows 54 % glucose conversion with 30 % fructose yield[7]. Similar conversion (48 %) and product yield (34 %, See SI Figure S7) were obtained when 40 mg of catalyst (UiO-66-MSBDC(20)) was used, which is still less than the quarter of the amount of Sn-beta catalyst (200 mg).

Tailor-made MOFs with desired functionalities have made it possible to achieve exceptionally efficient catalysts for glucose isomerization in water. UiO-66-MSBDC catalysts containing dual acidity, Lewis and Brønsted, provide exceptional product selectivity of around 90 % for glucose conversion into fructose and HMF reaching the performance of Sn-beta zeolite. Other MOF catalysts reported in the literature for glucose isomerization use either frameworks constructed from toxic metals (e.g., chromium[23-26]) and/or have been used in non-aqueous solvents that are toxic or flammable (e.g. DMSO or THF[27]). Our results show that UiO-66-MSBDC(y) catalysts are highly promising for scale-up because as well as operating in aqueous conditions and being recyclable, their synthesis does not require the toxic and corrosive conditions with a simple protocol and short duration. Scale-up of MOF synthesis using continuous flow reactors, often using water as a reaction medium, makes this a realistic prospect.[28] Enzymes including metal centres and basic histidine moieties possessing multi-functional capabilities are Nature's catalysts providing high selectivity at the expense of slow reactions and sensitive operational systems. Future work on the MOF catalysts will be devoted towards the better understanding of the active sites of this catalyst and the mechanism of their activity to optimize the product distribution, and their long-term stability in industrially relevant flow chemistry conditions.

Experimental Section

Synthesis of catalysts: UiO-66 was prepared by mixing 2.481 g zirconium chloride (Alfa Aesar), 3.54 g 1,4-benzenedicarboxylicacid (Sigma Aldrich), 100 ml *N*,*N*-dimethylformamide (Fisher Scientific) and 20 ml hydrochloric acid (37 %, VWR). The synthesis mixture was then transferred to a PTFE-lined autoclave and heated to 120 °C for 24 h. Afterwards, materials were filtered, washed with methanol and dried in air at 70°C. UiO-66-MSBDC(y) catalysts were prepared by substituting the benzene-1,4-dicarboxylic acid with monosodium 2-sulfo-benzene-1,4-dicarboxylate (TCI Chemicals). Catalytic activity tests: Catalyst (10 mg) was placed in a reaction vial (4 ml) with a magnetic stirring bar and 10 wt. % aqueous glucose solution was added. The vial was closed and placed in a preheated oil bath at 140 °C for 3 h. The reaction was quenched at 0°C and the product mixture analysed by HPLC. Characterisation of catalysts: Powder XRD data were collected using a Panalytical X'Pert Pro MPD equipped with monochromatic Cu Kα1 radiation and a PIXcel solidstate detector. Micrographs and elemental maps were obtained using a Zeiss Gemini scanning electron microscope with a large are SDD EDX detector, operating at 5 keV. Nitrogen adsorption isotherms were measured at -196°C on a Micromeritics ASAP2020 system. The samples were outgassed at 150°C for 12 h prior to the sorption measurements. Infra-red spectra were recorded using a Perkin Elmer Paragon 1000 FT-IR Spectrometer in attenuated total reflection mode. Thermogravimetric analysis (TGA) was performed using a Mettler Toledo Systems TGA/DSC 1 instrument under a constant flow of air (50 mL/min). Elemental analysis was performed by Medac Ltd (UK) for Zr and S using ICP-OES after digestion and for CHN using combustion. Extended experimental details can be found in the supporting information.

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Keywords: biomass • MOF • HMF • catalyst • UiO-66

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Entry for the Table of Contents

Highly selective glucose conversion into fructose and 5-hydroxymehtyl furfural over metal-organic framework catalyst (UiO-66-MSBDC). It operates in water at little over 100 °C, providing benign conditions with non-toxic reagents. It is recyclabile and constructed from a readily available and inexpensive organic ligands.