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Systematic modification of UiO-66 metal-organic frameworks for glucose conversion into 5-hydroxymethyl furfural in water

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Supporting information for this article is given via a link at the end of the document.

Abstract: Metal organic framework UiO-66 is studied as an adaptable heterogeneous catalyst for glucose conversion. UiO-66 was modified by: i) partial linker substitution, ii) particle size modulation and iii) linker defects. We studied the effect of crystallinity and functional groups on the glucose conversion and product yields. The main products are: i) fructose from the isomerisation of glucose, ii) mannose from the epimerisation of glucose and iii) 5-hydroxymethyl furfural from the dehydration of fructose. We found that defective and nano crystalline UiO-66 catalyst performs best for isomerisation. When 50 % of the linkers of UiO-66 are replaced by a sultonate-containing linker, the catalyst shows higher isomerisation activity than other UiO-66 catalysts. Naphthalene-dicarboxylate linkers were introduced to induce hydrophobicity and this catalyst further increased isomerisation activity showing 31 % fructose selectivity. Finally, the promising catalysts were tested in a flow reactor and a bifunctional mixed linker catalyst possessing both hydrophobic and acidic functional groups is shown to be stable in a time-on-stream study.

Introduction

Efficient harnessing of cellulosic biomass, a cheap and plentiful resource, could play a key role in reducing our dependence on fossil fuels. Among the current platform molecules derived from biomass, 5-hydroxymethyl furfural (HMF) has been considered as a promising intermediate compound for chemical industries to adopt biomass conversion into commodity chemicals. However, the cost of HMF production is still notably higher than that of fossil-fuel based manufacturing routes. Therefore, cost-effective chemical processes for HMF synthesis are highly desirable.

The highly selective production of HMF from fructose has been well documented. Meanwhile, HMF from the most abundant carbohydrate in cellulosic biomass, glucose, remains challenging. The fine tuning of the structure of catalysts for glucose utilisation is crucial to control the selectivity towards desired products. In this respect, metal-organic-frameworks (MOFs) form a promising class of catalytic materials, which have been coined “designer catalysts”. The combinations of metals and organic linkers give flexibility in tuning their structure and properties to introduce desired catalytic functionalities. Specifically, for glucose conversion, it can be envisaged that both Lewis acid sites and Brønsted acid sites can be engineered in a single solid host structure. Various MOFs have now been reported for the conversion of glucose including, MIL-101, UiO-66, an Yb-benzene-1,4-dicarboxylate, NU-1000, ZIF-8, MIL-100, MIL-53, MIL-88B. Hatton and co-workers prepared polymer composites of MIL-101 in which active bromine sites in the polymer allowed catalytic activity to be optimised for the conversion of D-fructose into HMF. Luo et al. studied the mechanism of glucose conversion over UiO-66 and found that UiO-66 can catalyse glucose isomerisation and epimerisation in aqueous media simultaneously and the catalytic behaviour is strongly dependent on the local coordination environment of the single site active centres in the framework. We have recently reported a UiO-66 MOF as heterogeneous catalyst for glucose conversion into HMF. The under-coordinated zirconium sites on the surface of the UiO-66 provide Lewis acid sites. This approach drives the first slow isomerisation step forward to allow formation of the desired product, HMF. To introduce the Brønsted acidity needed for fructose dehydration, we partially replaced the linker, benzene-1,4-dicarboxylate (BDC) in the UiO-66 MOF with 2-monsulfo-benzene-1,4-dicarboxylate (MSBDC). The catalysts showed fructose and HMF yields of 22 % and 6 %, respectively, with glucose conversion of 31 % in water alone with no requirement for additional mineral acid.

The stability of a catalyst is crucial for determining its potential applicability on large scale biomass conversion process. Stable in water under moderate conditions (<200 °C), this catalyst was recyclable over the course of four consecutive runs. Another advantage of UiO-66 is that it can also be produced in continuous flow using a commercially available linker.

In this study, we have greatly expanded the work on UiO-66 MOF as a heterogeneous catalyst in glucose isomerisation for HMF production. UiO-66, with ideal chemical formula Zr6O4(OH)4(BDC)6, where BDC = benzene-1,4-dicarboxylate, is one of the most stable MOFs known, both thermally and in
aqueous conditions, and has already been produced in various modified forms by addition of functional groups to the BDC linkers. Here, we have used UiO-66 as a backbone and investigated systematic modification of this water-stable MOF. Our aim was to use the possibility of forming isostructural MOFs with modified organic linkers to make a systematic investigation of their resulting catalytic properties. To our knowledge, so far only the sulfonic acid modified UiO-66 has been studied in this respect for glucose conversion and there is the likelihood of further optimisation of its catalytic performance with study of a wider range of linker substitutions. We have therefore explored the effects of defective sites, crystallinity and linker substitution on catalytic performance. The recyclability of UiO-66 catalysts was tested, as well as their performance over time in a flow reactor. Finally, the performances of the catalysts are compared with fructose when it is used as the starting carbohydrate reactant.

Results and Discussion

Structure and morphology of catalysts. Introducing high quantities of MSBDC linker into the framework UiO-66 can have a detrimental effect on the material's stability. To ensure a stable structure for the purpose of heterogeneous catalysis, the quantity of MSBDC linker within UiO-66 was limited to 20 % in our previous work. In this study, we have explored the limits of MSBDC linker substitution with respect to hydrothermal stability. PXRD analysis (Figure 1a) reveals that materials containing both 50 % and 100 % MSBDC linker can be successfully made. However, upon completion of a hydrothermal stability test at 140 °C, materials with MSBDC linker above 50 % experience a clear loss in crystallinity whereas MSBDC(50)-UiO-66 remains unchanged (Figure S1, Supporting Information). As such, we considered only materials containing an MSBDC linker content of 50 % or less for catalysis. For all of the samples prepared and discussed below, the actual amount of modified linker was measured using post-synthesis digestion NMR (Figure S15 and Table S3, Supporting Information), but the samples are named according to the intended linker content, since the digestion analysis showed consistent trends in linker content.

The diffraction patterns produced by MSBDC containing nano materials appear broadened but clearly resemble the inherent structure of UiO-66. PXRD analysis was also used to observe the crystallinity of all other materials prepared in this study. The PXRD

![Figure 1. Powder XRD patterns of a) MSBDC functionalised UiO-66 materials; b) UiO-66, defective UiO-66, nano UiO-66, ultra-nano UiO-66, and poorly crystalline UiO-66; c) nitro and amine groups functionalised UiO-66 materials.](image-url)
patterns of the standard UiO-66 and its variants are given in Figure 1b. The diffraction patterns of defective, nano, and ultra-nano materials revealed characteristic Bragg peaks of UiO-66, however, significant peak broadening is evident in the nano and ultra-nano samples. This peak broadening is indicative of the smaller crystallite domain sizes of these samples. This is confirmed by TEM images (Figure S10, Supporting Information) and small-angle X-ray scattering (Figure S16 and Table S6, Supporting Information) that show an obvious decrease in particle size for all the nanocrystalline materials compared to the standard UiO-66 sample. The synthesis of poorly crystalline UiO-66 was also successful, and consistent with the literature, only very broad peaks are present within the materials’ diffraction pattern.[18] Meanwhile, the diffraction pattern of defective UiO-66, shows sharp peaks. Mass losses quantified by TGA are given in Table S5, Supporting Information. The ideal chemical formula of UiO-66 is Zr6O4(OH)4(μ3-O)(μ4-O)(BDC)8·xH2O, with 6 BDC linkers per Zr6 cluster (n = 6).[19] It is known, however, that ligand defects are common in the materials and a more general chemical formula Zr6O4(OH)4(BDC)n·xH2O, with n BDC linkers per Zr6 cluster (n = 5–6)·xSolvent is appropriate. For our UiO-66 sample n = 5.45, thus suggesting that the material contains fewer linkers than the number of Zr6 clusters indicating a defective crystal structure (Table S5, Supporting Information). This is commonly the case for UiO-66.[20] The post synthesis hydrothermal treatment of UiO-66 resulted in a defective material with an even lower ligand content (n = 3.93). The nano UiO-66 material also showed a highly defective structure with n = 4.28. In the case of ultra-nano UiO-66, a value of n = 2.17 was obtained. Interestingly, the poorly crystalline nano material has a ligand content similar to the standard UiO-66.

The PXRD patterns of amine and nitro group functionalised materials are given in Figure 1b. The increasing quantities of amine functionalised linker reduces the crystallinity of the material. In fact, a complete substitution of BDC linker for the amine functionalised variant is known to result in a poorly crystalline material with only very broad diffraction features.[21] The introduction of nitro groups within the framework of UiO-66 also reduces crystallinity. However, the extent of this reduced crystallinity appears independent to the quantity of nitro-functionalised linker introduced into the framework.

The crystallinity of UiO-66 appears to be unaffected by the introduction of varying amounts of the functional groups of isophthalic acid (IPA), sulfobenzoic acid (3-sulfoben and 4-sulfoben), and naphthalene (naphtha) (Figure 2 a-c). It is worth noting that a sharp additional peak at around 17 degrees is present in the PXRD patterns of materials containing 10 % and 30 % isophthalic acid (Figure 2 a), which is presumably caused by residual acid form of the linker that was not washed from the MOF particles. From TGA data, along with digestion NMR to determine the amount of modified linker present (see Supporting Information), the number of ligands per zirconium cluster were obtained between n = 5 and n = 6. Similar values were found for MSBDC, nitro, amine, and naphthalene functionalised UiO-66 materials (Table S5, Supporting Information). The linker content of nano materials containing 20 % and 50 % MSBDC is calculated as n = 5.61, and 4.49, respectively. Interestingly, the introduction of IPA functionalised linker did not significantly increase defectiveness and the materials were less defective than standard UiO-66 (n = 5.7-6.0).

The diffraction patterns indicate the successful synthesis of MSBDC(50)-naphtha(50)-UiO-66 (Figure 2c). The introduction of hydroxyl groups within the framework of UiO-66 using the 2,5-dihydroxyterephthalate linker, did not appear to impact crystallinity. Meanwhile, the introduction of carboxylic acid groups using the benzene-1,2,4,5-tetracarboxylate linker (BTeC), resulted in a more amorphous material.

Figure 2. Powder XRD patterns of UiO-66 materials modified by: a) isophthalic acid (IPA), b) sulfobenzoic acid (3-sulfoben and 4-sulfoben), and c) naphthalene (naphtha).
Supporting Information

The incorporation of new ligands in the UiO-66 materials was analysed by FTIR spectroscopy. The FTIR spectra of UiO-66 and functionalised materials are given in the Supporting Information, Figures S2-7. The incorporation of sulfonic acid groups in materials containing the MSBDC linker was confirmed by the appearance of new bands at 620 cm\(^{-1}\), 1078 cm\(^{-1}\), 1180 cm\(^{-1}\), and 1223 cm\(^{-1}\) (Figure S2, Supporting Information), which correlate to the bending and stretching vibrations of the S=O and S-O bonds.[22] Specifically, peaks at 1180 cm\(^{-1}\) and 1223 cm\(^{-1}\) correspond to S=O bond vibrations, while peaks at 1078 cm\(^{-1}\) and 620 cm\(^{-1}\) correspond to S-O bond vibrations. In nitro-group functionalised UiO-66 materials, new bands appear at 1530 cm\(^{-1}\) and 1346 cm\(^{-1}\) which confirms their successful incorporation. These new bands correlate respectively to the asymmetric and symmetric stretching of (NO) modes (Figure S3, Supporting Information).[23] The presence of amine groups in NH\(_2\)-UiO-66 was confirmed by the appearance of new bands at 3457 cm\(^{-1}\) and 3376 cm\(^{-1}\) (Figure S4, Supporting Information). Here new bands correlate to the asymmetric and symmetric stretching of N-H nodes.[24] The introduction of isophthalic acid (IPA) results in a prominent peak at 1659 cm\(^{-1}\) (Figure S5, Supporting Information). It is worth noting that numerous other distinctive bands also appeared following the introduction of IPA. Specifically, these bands appear at 1092 cm\(^{-1}\), 2452 cm\(^{-1}\), 2771 cm\(^{-1}\), and at 2970 cm\(^{-1}\).[25] It is also possible that this could be due to the unreacted acid observed in the XRD of the 10 % and 30 % isophthalic acid containing materials. The FTIR spectra of UiO-66 and BTeC-UiO-66 contain a peak at 1710 cm\(^{-1}\) (Figure S6, Supporting Information). This peak of the BTeC material is consistent with the carboxylic acid groups on the linker’s aromatic ring.[26] The introduction of a single hydroxyl group on the linker aromatic ring is reported to generate bands at low wavelengths (450-750 cm\(^{-1}\)), as well as a band at 3300 cm\(^{-1}\) and a strong peak at 1240 cm\(^{-1}\).[27] Here we also find that the introduction of hydroxyl groups generates a strong peak at 1230 cm\(^{-1}\) and a band at around 3240 cm\(^{-1}\) (Figure S6, Supporting Information). Furthermore, the introduction of hydroxyl groups was also found to generate strong peaks at 869 cm\(^{-1}\), 1459 cm\(^{-1}\), 2446 cm\(^{-1}\), 2771 cm\(^{-1}\), 2928 cm\(^{-1}\), and 2968 cm\(^{-1}\).

The introduction of 3-sulfobenzoic acid and 4-sulfobenzoic acid into the framework of UiO-66 generated a band at 1035 cm\(^{-1}\) (Figure S7, Supporting Information). Furthermore, a small band appears at 615 cm\(^{-1}\) in the spectra of materials containing 3-sulfobenzoic acid. Meanwhile, the introduction of 4-sulfobenzoic acid produces additional bands at 1011 cm\(^{-1}\) and 1118 cm\(^{-1}\), which can be attributed to the presence of sulfobenzoic acid within the framework of UiO-66.

The BET surface areas of the materials are given Table S1 (Supporting Information). The BET surface areas of UiO-66 and defective UiO-66 are comparable; 737 m\(^2\)·g\(^{-1}\) and 722 m\(^2\)·g\(^{-1}\), respectively. Increasing amounts of MSBDC initially give an increased surface area, which may be due to increased defect concentration, but higher amounts give lower surface area owing to the presence of the bulk substituents on the linker, which counteract increased defects and lead to pore blocking. IPA, and naphthalene-functionalised linkers within the structure of UiO-66, were found to reduce surface area. This may be a result of functional groups or associated residual solvent blocking the materials’ pore network. As expected, the BET surface area of nano UiO-66 was found to be significantly larger than that of UiO-66 (1099 m\(^2\)·g\(^{-1}\)). However, the introduction of MSBDC linker within nano materials reduced BET surface area and micropore volume whilst increasing mesopore volume. This reduction in micropore volume may indicate that functional groups are blocking the materials pore network. The introduction of sulfobenzoic acid generally increased surface areas and micropore volumes in comparison to UiO-66. This is expected since these monocarboxyate linkers replace the bridging BDC ligand leading to greater free-pore volume.

The sulfur content of relevant materials and the molar ratio of sulfur to zirconium are shown in Table S2 (Supporting Information). It is observed that the MSBDC was successfully introduced into UiO-66 and nano UiO-66. In the ideal UiO-66 crystal structure UiO-66; Zr\(_6\)O\(_4\)(OH)\(_4\)(BDC)\(_4\), there is expected to be one mole of linker per zirconium. Therefore, when 10 % of BDC linker is replaced with MSBDC, it is expected that the sulfur to zirconium molar should be 1:0.1, and similar measured values are seen for MSBDC-UiO-66 and nano-MSBDC-UiO-66 materials. The sulfobenzoic acid functionalized UiO-66 materials show less sulfur to Zr ratio than the intended ligand substitution. This suggests that sulfobenzoic acid is not easy to introduce into the framework of UiO-66 and only a limited amount of sulfobenzoic acid can be incorporated. This is confirmed by digestion NMR that shows the amount of modified linker is smaller than expected (Supporting Information, Table S3).

**Glucose conversion reactions.** The glucose conversion and product yields over catalysts are given in Tables 1 and 2. The isomerisation of glucose to fructose is expected to be catalysed by the presence of Lewis acid sites.[28] In the case of UiO-66, defects at the Zr\(_6\)O\(_4\)(OH)\(_4\) clusters are believed to provide the necessary Lewis acidity for the isomerisation reaction.[29] UiO-66 was found to generate a glucose conversion of 16.3 % and a total product yield (fructose, mannose, HMF) of 5.6 % where the reactions were conducted in water at 140 °C for 3 h (Table 1, Entry 2). In addition to the products of fructose, mannose and HMF, several by-products may also form in glucose conversion reactions, and the mass balances are often not closed. The main by-products are usually classified as poorly characterised oligomers, named as humins, that precipitate as solids and are not analysed with the small molecule products.[30] In addition, retro-aldolization of carbohydrates, formation of lactic acid,urfural, and levulinic acid may also be observed with an overall deficit in mass balance.[32] Increasing the number of available defective Zr sites is expected to increase the catalytic activity of UiO-66 and result in greater fructose yields. Indeed, defective-UiO-66 results in a glucose conversion of 21 % and a total product yield of 11 % (Table 1, Entry 3). Moreover, the defective material more than doubled the fructose yield whilst increasing mannose yield by almost seven to eight-fold. The increase in mannose production is the result of glucose epimerisation.

Studies on the nature of the active Sn sites in zeolite beta, which has been used for glucose conversion, widely agree that the reactions take place on open metal sites.[31] Partial hydrolysis of a fully coordinated tetrahedral {SnO\(_4\)} sites is believed to generate an open site, where Sn is present as [{SnO\(_2\)}Sn(OH)] with an adjacent silanol group (Si-OH).[32] Both open and closed sites can coordinate two molecules of water, changing the tetrahedral coordination into octahedral, and these can subsequently be replaced by glucose that coordinates directly to the Lewis-acidic silicon. The adjacent silanol groups are
significant in stabilising the transition state that allows isomerisation to fructose. The role of the silanol groups as

\[
\text{Fructose} \rightarrow \text{Mannose} \rightarrow \text{HMF}
\]

Table 1. Glucose conversion reactions over UiO-66 and MSBDC functionalised UiO-66 catalysts.\(^a\)

| Entry | Catalyst          | Conversion (%) | Fructose | Mannose | HMF | Total | Selectivity (%) |
|-------|-------------------|---------------|----------|---------|-----|-------|-----------------|
| 1     | No catalyst       | 5.6           | 0.8      | 0.0     | 2.1 | 2.9   | 14.3            | 0.0             | 37.5 |
| 2     | UiO-66            | 16.3          | 1.6      | 0.5     | 3.5 | 5.6   | 9.8             | 3.1             | 21.5 |
| 3     | Defective UiO-66  | 21.0          | 3.8      | 3.9     | 3.3 | 11.0  | 18.1            | 18.6            | 15.7 |
| 4     | Nano UiO-66       | 27.5          | 4.2      | 5.3     | 4.0 | 13.5  | 15.3            | 19.3            | 14.5 |
| 5     | Ultra-nano UiO-66 | 29.8          | 5.0      | 6.1     | 4.4 | 15.5  | 16.8            | 20.5            | 14.8 |
| 6     | Poorly crystalline | 26.3          | 4.6      | 3.8     | 4.8 | 13.1  | 17.5            | 14.4            | 18.3 |
| 7     | MSBDC(10)-UiO-66  | 25.5          | 4.6      | 3.9     | 4.0 | 12.6  | 18.0            | 15.3            | 15.7 |
| 8     | MSBDC(20)-UiO-66  | 30.7          | 5.7      | 6.2     | 5.0 | 16.9  | 18.6            | 20.2            | 16.3 |
| 9     | MSBDC(50)-UiO-66  | 37.3          | 8.1      | 7.3     | 6.5 | 22.0  | 21.7            | 19.6            | 17.4 |
| 10    | Nano MSBDC(20)-  | 37.8          | 6.3      | 6.8     | 6.9 | 20.0  | 16.7            | 18.0            | 18.3 |
| 11    | Nano MSBDC(50)-  | 39.1          | 6.4      | 6.8     | 7.7 | 20.9  | 16.4            | 17.4            | 19.7 |
| 12    | 3-sulfoben(20)-  | 24.5          | 4.0      | 3.7     | 3.6 | 11.3  | 16.3            | 15.1            | 14.7 |
| 13    | 3-sulfoben(40)-  | 27.0          | 4.3      | 4.2     | 4.3 | 12.8  | 15.9            | 15.6            | 15.9 |
| 14    | 4-sulfoben(20)-  | 27.2          | 4.8      | 3.5     | 4.1 | 12.3  | 17.6            | 12.9            | 15.1 |
| 15    | 4-sulfoben(40)-  | 28.0          | 5.0      | 4.2     | 4.1 | 13.3  | 17.9            | 15.0            | 14.6 |

\(a\) Reaction conditions are: 140 °C, 3 h, substrate concentration of 100 mg·mL\(^{-1}\), Glucose to catalyst ratio of 30:1 by weight.

Brensted bases has also been speculated, but when the adjacent silanol groups act as spectators, the formation of mannose through a carbon shift, i.e. the epimerisation of glucose, is favoured.\(^{[33]}\) Therefore, we propose that over UiO-66, the hydroxyl groups present in the \(\{\text{Zr}_{6}\text{O}_{4}(\text{OH})_{12}\}\) clusters play a different role to the silanol groups in Sn-beta, and largely act as spectators, since the Lewis acid centres on UiO-66 preferentially catalyse the epimerisation route towards mannose.

To examine the effects of crystal size and morphology on catalytic performance, nano UiO-66, ultra-nano UiO-66, and poorly crystalline UiO-66 materials were studied. The use of nano and ultra-nano materials resulted in glucose conversions of 27.5 % and 29.8 % respectively; each considerably higher than that produced by the standard UiO-66 material (Entries 4 and 6). The observed increase in activity could be attributed to the combination of a higher number of defective Zr sites and larger external surface areas. The catalytic activity of poorly crystalline UiO-66 was only marginally lower than the other nanocrystalline materials despite its less crystalline nature. This may indicate that glucose does not enter the pores of UiO-66 and instead reactions are taking place on the outer surface of the material. Indeed, recent work by de Mello and Tsapatsis suggests that glucose is unable to enter the structure of un-modulated UiO-66, i.e. UiO-66 that does not have missing Zr clusters.\(^{[56]}\) The nano and ultra-nano materials generated higher quantities of fructose, mannose and HMF than UiO-66. Within these product distributions, similar quantities of mannose were produced. Given the defectiveness of the nano materials, this provides further evidence that increasing the number of defective Zr sites within UiO-66 effectively promotes mannose production.

In our previous study we explored the use of sulfonic acid functionalised UiO-66 as an isomerisation catalyst in water.\(^{[56]}\) Consistent with literature, the introduction of electron withdrawing sulfonic acid groups was found to increase the Lewis acidity of UiO-66; ultimately resulting in greater glucose conversions and higher ratio of fructose to mannose in product yields.\(^{[56, 34]}\) The addition of Brensted acid sites may also facilitate the dehydration of fructose to 5-HMF. Increasing the quantity of the MSBDC linker (Table 1, Entry 2) in UiO-66 improves catalytic activity (Table 1, Entry 7-9). Specifically, MSBDC(50)-UiO-66 gave a glucose conversion of 37.3 % and an overall product yield of 22 %, making it the most selective material. Comparing the product distributions of MSBDC containing materials to standard UiO-66 reveals that the greatest increase in yield is seen across fructose and mannose, rather than HMF. This suggests that the introduction of sulfonic acid groups in UiO-66 primarily promotes both the isomerisation and epimerisation reactions, rather than dehydration of fructose towards HMF production. One explanation could be that MSBDC-UiO-66 contains more Lewis acid sites, by the structure being more defective, instead of significantly increasing the Brensted acidity in the vicinity of Lewis acid sites necessary to drive the reaction towards isomerisation.
followed by dehydration to HMF. To test this, we synthesised nano MSDBC-UIO-66 materials. As seen in Table 1, nano MSDBC(20)-UIO-66 (Table 1, Entry 10) generated the highest glucose conversion and a total product yield than the parent MSDBC(20)-UIO-66 material (Table 1, Entry 8). In addition, it shows a significantly higher conversion and yield than standard UiO-66. The higher activity of the nano MSDBC(20)-UIO-66 material can therefore be attributed to its higher number of defective Zr sites (i.e., Lewis acid centres). The comparison of MSDBC(50)-UIO-66 materials (Table 1, Entries 9 and 11) are in line with these findings. The nano MSDBC(50)-UIO-66 catalyst gives a slightly higher conversion than MSDBC(50)-UIO-66 catalyst as expected; accompanied by a higher HMF production (6.5 % vs 7.7 %). However, the effect of crystal size and sulfur addition were less dramatic since MSDBC(50)-UIO-66 generates more overall product yield.

The introduction of the sulfobenzoate linker in UiO-66 has a dual effect of increasing the number of defective zirconium sites within the MOF whilst also providing sulfonic acid functional groups. We considered both 3-sulfobenzoic acid and 4-sulfobenzoic acid linkers. As seen in Table 1, the introduction of sulfobenzoate increased both glucose conversion and product yields when compared to standard UiO-66. Moreover, increasing the quantity of sulfobenzoic acid linker within the framework of UiO-66 from 20 % to 40 % resulted in a slight increase in catalytic activity. This is expected, as ICP analysis revealed that the 40 % containing material contains only slightly more sulfobenzoic acid than the 20 % material. It is inferred that sulfobenzoate linker is not easy to introduce into the framework, and a higher quantity of this linker in the synthesis mixture instead impairs its successful incorporation into the UiO-66 framework.

The results obtained from the use of nitro, BTeC, IPA, amine, and naphthalene functionalised UiO-66 are summarised in Table 2. Linkers containing strong electron-withdrawing nitro groups were introduced into the UiO-66 framework at various ratios. These are expected to increase the strength of the Lewis acidity of the under-coordinated Zr centres. On the contrary, the introduction of nitro functionalised linker into the framework of UiO-66 did not appear to significantly improve glucose conversion (Table 2, Entries 1-3). The lower activity of the nitro functionalised materials, as compared to MSDBC functionalised materials, could suggest that strong Lewis acidic Zr sites are unfavourable for glucose isomerisation. It should also be noted that the low BET surface areas for these materials is also an important factor for low conversion of glucose isomerisation, and this may be due to trapped solvent interacting strongly with the ligand functional groups making it difficult to remove.

Moderate electron-withdrawing groups in the form of carboxylic acid (BTeC) were also introduced into the UiO-66 framework, and they also provide Brønsted acid sites. The presence of these carboxylic acid groups within the material generated an HMF yield of 7.3 % (Table 2, Entry 4). This HMF yield suggests that carboxylic acid groups within BTeC-UIO-66 are providing sufficient Brønsted acidity to promote the dehydration towards

### Table 2. Glucose conversion reactions over UiO-66 and nitro, BTeC, amine, IPA, and naphtha functionalised Uio-66 catalysts.

| Entry | Catalyst | Conversion (%) | Yield (%) | Selectivity (%) |
|-------|----------|----------------|-----------|-----------------|
|       |          | Fructose | Mannose | HMF | Total | Fructose | Mannose | HMF |
| 1     | NO$_2$(20)-UIO-66 | 16.8 | 1.6 | 0.3 | 4.7 | 6.6 | 9.5 | 1.8 | 28.0 |
| 2     | NO$_2$(50)-UIO-66 | 19.9 | 2.1 | 0.6 | 5.6 | 8.3 | 10.6 | 3.0 | 28.1 |
| 3     | NO$_2$(100)-UIO-66 | 21.9 | 3.0 | 1.2 | 5.5 | 9.7 | 13.7 | 5.5 | 25.1 |
| 4     | BTeC-UIO-66 | 20.9 | 2.0 | 0.3 | 7.3 | 9.7 | 9.6 | 1.4 | 34.9 |
| 5     | IPA(10)-UIO-66 | 23.6 | 2.8 | 3.7 | 4.7 | 11.2 | 11.9 | 15.7 | 19.9 |
| 6     | IPA(20)-UIO-66 | 23.6 | 2.7 | 3.6 | 4.5 | 10.8 | 11.4 | 15.3 | 19.1 |
| 7     | IPA(30)-UIO-66 | 23.1 | 2.7 | 3.8 | 4.6 | 11.1 | 11.7 | 16.5 | 19.9 |
| 8     | IPA(40)-UIO-66 | 24.4 | 3.1 | 4.1 | 4.9 | 12.1 | 12.7 | 16.8 | 20.1 |
| 9     | NH$_2$(20)-UIO-66 | 16.7 | 2.2 | 1.4 | 3.9 | 7.5 | 13.2 | 8.4 | 23.4 |
| 10    | NH$_2$(50)-UIO-66 | 19.0 | 1.9 | 1.2 | 5.2 | 8.3 | 10.0 | 6.3 | 27.4 |
| 11    | NH$_2$(100)-UIO-66 | 15.9 | 0.9 | 0.2 | 5.5 | 6.6 | 5.7 | 1.3 | 34.6 |
| 12    | Naphtha(20)-UIO-66 | 18.0 | 4.7 | 0.8 | 3.2 | 8.6 | 26.1 | 4.4 | 17.8 |
| 13    | Naphtha(50)-UIO-66 | 18.2 | 5.5 | 0.9 | 3.1 | 9.5 | 30.2 | 4.9 | 17.0 |
| 14    | Naphtha(100)-UIO-66 | 21.2 | 6.6 | 1.2 | 3.7 | 11.6 | 31.1 | 5.7 | 17.5 |
| 15    | MSDBC(50)-naphtha(50)-UIO-66 | 32.7 | 7.1 | 5.4 | 5.4 | 17.9 | 21.7 | 16.5 | 16.5 |
| 16    | Hydroxy-UIO-66 | 23.8 | 5.2 | 2.2 | 4.9 | 12.3 | 21.8 | 9.2 | 20.6 |

*Reaction conditions are: 140 °C, 3 h, substrate concentration of 100 mg mL$^{-1}$, Glucose to catalyst ratio of 30:1 by weight.
HMF production. However, like the nitro functionalised materials, the incorporation of carboxylic acid groups did not increase the total glucose conversion like MSBDC-UIO-66 materials. The addition of these functional groups to moderate the Lewis acidity of catalysts through their electron-withdrawing strength are less effective than sulfonic acid for glucose conversion. To combine the catalytic activity of highly defective materials with the Brønsted acidity (and hence dehydration capability), isophthalate (IPA) was introduced into the UIO-66 framework. Its incorporation within UIO-66 could provide the presence of both carboxylic acid groups and defective zirconium centres. However, TGA results showed that (Table S5, Supporting Information) the introduction of IPA into the framework of UIO-66 did not significantly increase the number of defective sites. This may suggest that the majority of IPA linker is bound to the outer surface of the UIO-66 crystals. Replacing 10 % of Uio-66 framework BDC linker with IPA generates a glucose conversion of 24 % and a total product yield of 11.2 % (Table 2, Entry 5). The effect of the IPA linker on catalytic performance appears to be maximised at this lower level of incorporation. Increasing the IPA content did not significantly improve catalytic performance (Table 2, Entries 6-8).

The effect of electron donating groups was studied through the introduction of amine functionalised linkers. The introduction of 20 % amine functionalised linker did not significantly improve glucose conversion when compared to standard UIO-66. Increasing the quantity of amine functionalised linker to 50 % did increase glucose conversion to 19 % (Table 2, Entry 9). Increasing the amine content further was found to reduce the catalytic activity (Table 2, Entry 11). This decline in activity may result from the electron-donating amine groups reducing the Lewis acidity of local Zr active sites within the material and there could be an optimum for the number of amine functional groups. One of the important factors for a highly selective catalyst is the hydrophobicity of the crystalline matrix, e.g., as seen in Sn-beta.[35] Although the exact reason is under discussion in the literature, the benefit partly comes from the fact that the hydrophobic matrix protects the active sites from deactivation through contact with bulk water[36] and is partly due to the ease of interaction of glucose with these active centres.[37] To study this effect a hydrophobic naphthalene-functionalised linker (Table 1, Entry 9) was introduced into the framework of UIO-66 at a ratio of 20 %, 50 %, or 100 %, relative to BDC. The resulting catalytic performances of these materials are shown in Table 2 (Entries 12 – 14). As seen, the conversion of glucose by Naphtha(20)-UIO-66 is comparable to that of UIO-66. However, the selectivity of the reaction towards fructose is improved, thus highlighting the benefits of hydrophobicity of the catalyst. More interesting than this, whilst fructose yields are improved by the presence of naphthalene, mannose yields remain comparable to that of the standard material. This suggests that the proximity of water to Zr active sites has a prominent impact on reaction selectivity for fructose. The absence (or decrease) of water around the active site, supresses the reaction pathway towards mannose whilst promoting that towards fructose. This could be due to the more freedom of glucose to coordinate to the Lewis acid Zr centres in a form which allows the adjacent proton rich sites to participate in the reaction similar to Sn-beta zeolite.[33] In the presence of water, the nearby sites could be saturated by water. To test this, a combination of naphthalene and sulfonic acid functionalised linkers was considered. The resulting activity of the dual linker functionalised material is shown in (Table 2, Entry 15). The bifunctional material, MSBDC(50)-naphtha(50)-Uio66 effectively doubled the glucose conversion as compared to standard Uio-66. However, the presence of sulfonic acid groups in the material makes it more defective such that the reaction pathway towards mannose was no longer suppressed to the same extent as with naphtha-Uio-66 materials. Nevertheless, it produced the highest fructose selectivity (22 %) among glucose conversions above 30 %.

It is reported in literature that in Sn-beta the participation of nearby silanol (Si-OH) groups to the reaction plays an important role for the stabilisation of the transition state and thus reduces the activation energy of isomerisation reaction.[28] We introduced hydroxyl groups to UIO-66 framework by using 2,5-dihydroxyterephthalic acid and the resulting catalyst, hydroxy-UIO-66, gave a glucose conversion of 23.8 % along with a 21 % selectivity towards HMF. This activity and selectivity highlight the benefits of the presence of OH groups.

The parent UIO-66 material is known to possess Lewis acid sites, and this has been well documented in the literature.[36a, 38] To prove the presence of acid sites in our materials we measured pyridine adsorption FTIR spectra, as shown in Supporting Information, Figures S11-13. This shows signature peaks of Lewis acid sites as well as Bronsted acid sites in line with literature.[39]

The catalysis results from the modified UIO-66 materials can be compared with other MOFs reported in the literature.[40] It is important to note that we have studied catalysis in water alone as a reaction medium, and while higher total conversions have been reported in non-aqueous solvents, such as THF or DMSO, conversions of ~40 % as observed here for the best performing materials are among the highest seen in aqueous conditions. For example, sulfonic acid modified MIL-101(Cr) shows a conversion of 21.6 % to give only fructose[41], and while the best material in water, NU-1000, gives a 60 % conversion, the yield of HMF is significantly less than we have found.[42]

Catalyst stability and recyclability. Three catalysts showing high glucose conversion and product selectivity towards fructose and HMF, namely BTeC-Uio-66, MSBDC(50)-Uio-66, and MSBDC(50)-naphtha(50)-Uio-66 were further studied in a series of recycle reactions (Figure 3). Each catalyst was recovered and reused after each reaction through a course of four consecutive reactions. After 4th reaction, the catalysts were analysed by PXRD to assess the materials’ stability (Figure S8, Supporting Information). The activity of each catalyst dropped following the first reaction cycle. This initial decline in activity could be due to a combination of several factors. Firstly, smaller, and highly active particles contained within the bulk catalyst are hard to recover and could be lost from the system after the first reaction cycle. Secondly, functional groups such as sulfonic acid could be removed from the catalyst during reaction. Alternatively, insoluble
carbon by-products, humins, could deposit on catalytically active Zr sites resulting in deactivation. The activity of BTeC-Uio-66 appeared to be the most resilient during catalyst recycling. However, the HMF yield declined over the course of consecutive reactions. This suggests that the carboxylic acid functional groups have been deactivated or removed from the material during the first reaction. The glucose conversions of MSBDC(50)-naphtha(50)-Uio-66 and MSBDC(50)-Uio-66 appears to stabilise at around 25 % following an initial drop. The stabilities of the other catalysts were assessed by recovering the materials post-reaction and analysing them via PXRD (Figure S9, Supporting Information). The crystallinity of IPA and sulfobenzoic acid containing Uio-66 is preserved during reaction, as is the crystallinity of nano-Uio-66. The functionalised amine material remains poorly crystalline and the nitro material likewise becomes poorly crystalline after the reaction.

Glucose conversion in flow reactor. For the purpose of scale up, the performance of catalysts should be explored in continuous flow in a packed bed reactor. The results of the flow reactor study is shown in Figure 4. At a low flow rate (0.14 ml·min⁻¹), Uio-66 generates an initial glucose conversion of 15 % and a fructose yield of 5 %. This initial conversion and fructose yield then decline slightly with increasing time on stream before finally stabilising. After 240 min on stream, the catalyst shows a glucose conversion of 13.5 % and a fructose yield of 4.5 %. This conversion and fructose yield are comparable to that seen at the beginning of the time on stream. This suggests that the activity of Uio-66 has not experienced significant deactivation under these reaction conditions and thus Uio-66 is a highly promising catalyst for scale-up. At a higher flow rate of 0.28 ml·min⁻¹, the activity of Uio-66 begins to decline after 150 min on stream. The deactivation observed here is likely linked to a build-up of humins on the surface of the Uio-66 catalyst. The formation of these carbon by-products is common within glucose isomerisation reactions. Indeed, the deactivation seen in Uio-66, could be same as is seen in Sn-beta. Due to the expected fragility of MOFs compared to zeolites, it could be possible that changes in the materials’ structure could occur under relatively mild conditions. The performance of MSBDC(50)-Uio-66 is shown in Figure 4, c-d. The activity of MSBDC(50)-Uio-66 gradually declined at both flow rates. Glucose conversion fell from 28.8 % to around 15.7 % 480 min. The deactivation of MSBDC(50)-Uio-66 observed could be related to the loss of functional groups from the catalyst thus eventually resulting in a similar fructose yield of around 5 % as Uio-66. The MSBDC(50)-naphtha(50)-Uio-66 generates an initial glucose conversion of around 36 %. This was accompanied by fructose and mannose yields of 9.3 % and 4.5 %, respectively. The performance of the catalyst declines before stabilising after 350 min of time on stream. This may suggest that sulfonic acid groups are removed from the material. Once stable, the catalyst delivers a constant glucose conversion of 22 % and a total product yield of 10.5 %. This catalytic activity is greater than that observed when using Uio-66 under the same reaction conditions. As such, the activity of the material suggests that although sulfonic acid groups may have been removed, the material still contains hydrophobic naphthalene functionalised linker that could produce higher catalytic performance than standard Uio-66. At a higher flow rate of 0.28 ml·min⁻¹, the catalytic activity of the material appears extremely stable. This may suggest that sulfonic acid groups are removed from the material quicker when a higher flow rate is applied (i.e., loss of sulfonic acid groups occurs before t = 30 min).
Figure 4. Catalytic activity of the catalysts in flow reactor, a) UiO-66, b) MSBDC(50)-UiO66 and c) MSBDC(50)-naphtha(50)-UiO-66. The upper and below chart show the results at flow rates of 0.14 ml·min⁻¹ and 0.28 ml·min⁻¹ respectively. Reactor contains 80 mg of catalyst under study. Temperature is kept at 140 °C and feedstock is 100 mg·mL⁻¹ glucose in water.

Fructose conversions. Fructose is known to be dehydrated to HMF in the presence of Bronsted acids, particularly mineral acids. To evaluate the dehydration capabilities of the materials considered, reactions were performed using fructose as the feedstock. The results of these reactions are shown in Table 3. The blank reaction generated a fructose conversion of 20.7 % and an HMF yield of 18.1 %. The autocatalytic nature of fructose dehydration in water has been previously reported in the literature and is thought to be catalysed by the formation of formic acid in the reaction solution.⁴³ UiO-66 generated a fructose conversion of 44.7 % along with an HMF yield of 33.2 %. This higher HMF yield suggests that UiO-66 is facilitating the dehydration of fructose to HMF. We expect that Bronsted acidity within UiO-66 may result from any uncoordinated -COOH groups of BDC within the material. In each MOF-catalysed reaction, small quantities of glucose were observed. Mannose was also generated in trace amounts in the majority reactions. Meanwhile, fructose and mannose were not formed in the blank reaction. The isomerisation of glucose is a reversible reaction, and therefore, the small quantities of glucose found here highlight the Lewis acidity of the UiO-66 catalysts. BTeC-UiO-66 generated an HMF yield of 40.2 %. This is the highest HMF yield generated in this series of reactions and suggests that the presence of sufficient free -COOH groups provide enough Bronsted acidity to catalyse the dehydration of fructose to HMF. However, the free -COOH groups in IPA functionalised UiO-66 were unable to effectively enhance HMF yields. This could also explain their relatively lower activity in glucose conversions.

Table 4 summarises some of the zeolites and MOFs previously reported in the literature for the single step conversion of glucose to HMF. It can be seen that the modified UiO-66 materials we have studied give comparable catalytic conversion and HMF selectivity to the optimum materials. As was mentioned above, zeolite Sn beta requires use of HCl to provide Bronsted acidity. [36a]. For some of the MOF catalysts, the glucose conversion is tuned by use of mixed aqueous-organic solvents, such as THF.⁷,⁴⁴ The advantage of the use of UiO-66 MOFs is their hydrothermal stability and ease of modification of linkers to produce catalysts that operate in water alone, without additional mineral acids or organic solvents, which would be less desirable in an industrial process.

Conclusion

UiO-66 MOFs catalyse the isomerisation of glucose to fructose to then produce the desired platform molecule HMF in aqueous conditions. The catalytic ability of these MOFs can be tuned through the introduction of structural defects, particle size modulation, and the incorporation of functional groups. The catalytic performance of UiO-66 can be improved by increasing the number of defective Zr sites within the framework. These
defective Zr sites are responsible for facilitating Lewis acid catalysed glucose isomerisation. The nano-Uio-66 materials can generate higher glucose conversions and desirable product yields than standard Uio-66. This improved catalytic performance can be attributed to the smaller particle size of the nano materials and their increased defectiveness inducing more under-coordinated zirconium centres, and thus more Lewis acid sites. The introduction of sulfonic acid containing MSBDC linker has the greatest impact on catalytic activity. The electron-withdrawing sulfonic acid groups are proposed to enhance the Lewis acidity of nearby defective Zr sites and could participate in the glucose isomerisation reaction step. Naphthalene groups enhance the reaction selectivity towards fructose by enhancing the hydrophobicity of the Uio-66 framework. Meanwhile, the introduction of free --COOH groups, through the incorporation of a BTeC linker, was found to increase the HMF yields – particularly in fructose dehydration. Several Uio-66 materials were tested in a series of recycle reactions. Each of these materials proved to be recyclable and stable in batch reactors. As such, the performances of selected Uio-66 catalysts were further studied in a purpose-built continuous flow packed bed reactor. The performance of MSBDC(50)-Uio-66 rapidly declines and the glucose conversion and product yields over this catalyst stabilise at levels comparable to standard Uio-66. This suggests that the sulfonic acid groups are removed from the material in continuous flow. On the other hand, the performance of Uio-66, and a naphthalene/MSBDC functionalised material, proved to be highly stable in continuous flow. As such, these catalysts warrant further study and could be of considerable interest for scale-up.

Table 3. Fructose conversion over Uio-66 catalysts. 

| Entry | Catalyst                  | Conversion (%) | Fructose | Yield (%) | Selectivity (%) |
|-------|---------------------------|----------------|----------|-----------|-----------------|
|       |                           |                | Mannose  | HMF       | Total           |
| 1     | None                      | 20.7           | 0.0      | 18.1      | 18.1            |
| 2     | Uio-66                    | 44.7           | 0.5      | 33.2      | 33.9            |
| 3     | Defective-Uio-66          | 34.6           | 0.8      | 20.1      | 21.3            |
| 4     | Nano-Uio-66               | 42.2           | 0.9      | 20.5      | 21.9            |
| 5     | MSBDC(10)-Uio-66          | 42.9           | 1.1      | 25.6      | 27.4            |
| 6     | MSBDC(20)-Uio-66          | 44.5           | 1.2      | 24.7      | 26.5            |
| 7     | MSBDC(50)-Uio-66          | 47.4           | 1.7      | 23.2      | 24.9            |
| 8     | Nano MSBDC(20)-Uio-66     | 46.0           | 1.4      | 22.2      | 24.2            |
| 9     | Nano MSBDC(50)-Uio-66     | 47.5           | 1.6      | 22.5      | 25.0            |
| 10    | 3-sulfoben(20)-Uio-66     | 40.1           | 1.0      | 20.8      | 21.8            |
| 11    | 3-sulfoben(40)-Uio-66     | 44.8           | 0.9      | 22.3      | 23.8            |
| 12    | 4-sulfoben(20)-Uio-66     | 42.2           | 1.1      | 22.0      | 23.8            |
| 13    | 4-sulfoben(40)-Uio-66     | 43.0           | 1.1      | 21.4      | 23.1            |
| 14    | No(20)-Uio-66             | 46.2           | 0.3      | 34.3      | 34.8            |
| 15    | No(50)-Uio-66             | 47.4           | 0.5      | 32.8      | 33.6            |
| 16    | No(100)-Uio-66            | 47.7           | 0.7      | 30.7      | 31.4            |
| 17    | BTeC-Uio-66               | 59.9           | 0.5      | 40.7      | 41.5            |
| 18    | IPA(10)-Uio-66            | 36.2           | 0.6      | 22.7      | 23.6            |
| 19    | IPA(20)-Uio-66            | 37.3           | 0.6      | 22.4      | 23.3            |
| 20    | IPA(30)-Uio-66            | 35.8           | 0.6      | 21.1      | 21.9            |
| 21    | IPA(40)-Uio-66            | 37.8           | 0.7      | 21.7      | 22.7            |
| 22    | NH(20)-Uio-66             | 46.9           | 0.5      | 35.2      | 36.0            |
| 23    | NH(50)-Uio-66             | 51.2           | 0.4      | 36.9      | 37.7            |
| 24    | NH(100)-Uio-66            | 40.0           | 0.3      | 28.8      | 29.3            |
| 25    | Naphtha(50)-Uio-66        | 37.1           | 1.2      | 22.1      | 23.9            |
Experimental Section

**Catalyst Synthesis.** UIO-66 was prepared by mixing 2.48 g zirconium tetrachloride (Alfa Aesar, anhydrous, 99 %), 3.54 g benzene-1,4-dicarboxylic acid (Sigma Aldrich, H₂BDC, Scheme 1), 100 ml N,N-dimethylformamide (DMF, Fisher Scientific) and 20 ml hydrochloric acid (37 % w/v, VWR). Then, the synthesis mixture was transferred into a Teflon®-lined autoclave (4748 large capacity acid digestion Vessel, 200 mL, Parr Instrument Company) and heated at 120 °C for 24 h. Next, the resulting material was filtered, washed with methanol and dried in air at 70 °C. Functionalised variants of UIO-66 were prepared by substituting fractions of benzene-1,4-dicarboxylic acid with alternative precursors (acids and salts) of linkers (anions) during synthesis, as shown in Scheme 1. The catalysts are named with the replaced linker and the percentage (acids and salts) of linkers (anions) during synthesis, as shown in Table 4. The catalysts are denoted by UIO-66, Naphtha(100) or MSDBC(50) depending on whether the benzene-1,4-dicarboxylic acid was replaced with functionalised variants of benzene-1,4-dicarboxylic acid, e.g. MSBDC(20) for MSDBC(50) and Naphtha(100) for Naphtha(100). All the linkers were replaced with functionalised versions. BTeC-UIO-66 catalyst was prepared by mixing...
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1.20 g ZrCl₄, 1.30 g benzene-1,2,4,5-tetracarboxylic acid (Sigma Aldrich) and 100 mL water. The synthesis mixture was then transferred into a Teflon™-lined autoclave (4744 G General Purpose Acid Digestion Vessel, 200 mL, Parr Instrument Company) and heated at 120 °C for 24 h. The autoclave was subsequently cooled and 30 mL of water was added to the resulting gel before it was reheated at 120 °C for a further 24 h under reflux. DEF1 Defective UiO-66 was prepared via hydrothermal extraction of linker from standard UiO-66 by hydrothermally treating 0.50 g of UiO-66 in 10 ml of water at 240 °C for 24 h. The extracted linker, in its acid form, was subsequently removed from the material by washing with DMF and then methanol. The washed material was dried in air at 70 °C. Nano UiO-66 materials were synthesised following the procedures reported in literature.[18] A pre-solution was prepared by aging ZrCl₄ (1.75 g) in DMF (75 ml), water (1.60 ml) and acetic acid (7 ml) for 48 h. Then, 0.33 g of benzene-1,4-dicarboxylic acid was mixed with 20 ml of the pre-made solution and heated in a Teflon™-lined autoclave (4744 General Purpose Acid Digestion Vessel, 45 mL, Parr Instrument Company) at 120 °C for 24 h. The resulting material was recovered, washed in methanol, and dried in air at 70 °C. An ultra-nano-Uio-66 material was synthesised following a similar procedure. To induce a smaller crystal size, the pre-solution was instead aged for 96 h. Finally, a poorly crystalline nano-Uio-66 was synthesised by following the same procedure of nano-Uio-66 as explained above without acetic acid and with increased water content to 3.2 mL.

Catalyst Characterisation. Powder X-ray diffraction (PXRD) patterns were recorded with a scanning speed of 0.05°·min⁻¹ on a Panalytical X'Pert Pro spectrometer equipped with a monochromatic Cu Kα radiation and a PIXcel solid-state detector. The PXRD patterns were fitted using the Le Bail method using the GSAS software[43] to obtain refined unit cell parameters with all materials assigned the cubic space group Fm̅3m. Thermogravimetric analysis (TGA) was performed in air using a Mettler Toledo Systems TGA/DSC 1 unit. Air flow during TGA was maintained at 50 ml·min⁻¹ while temperature was ramped at 10 °C·min⁻¹. Fourier transform infra-red (FTIR) spectra were recorded using a Perkin Elmer Paragon 1000 FTIR spectrometer in attenuated total reflection mode. Nitrogen sorption isotherms were measured at -196 °C on a Micromeritics ASAP2020 instrument in static measurement mode. The samples were outgassed at 110 °C for 12 h prior to the sorption measurements. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area (S_BET) from the adsorption isotherm data obtained between p/p₀=0.05 and 0.25. The total pore volume (V_BET) was calculated at p/p₀ = 0.97. The mesopore volume (V_MESO) and mesopore size distribution were calculated using the Barrett-Joyner-Halenda (BJH) method on the adsorption branch of the isotherm. The micropore volume (V_MICRO) was calculated from the t-plot curve at thickness range between 3.5 and 5.4 Å. The sulfur and zirconium elemental composition of materials were determined by the inductively coupled plasma optical emission spectrometry (ICP-OES, Varian Vista MPX) method after digestion in concentrated nitric acid. The error margins for elemental analysis are 0.3 %. Transmission electron microscopy was performed using a double corrected ARM200F microscope operating at 200 kV.

Catalytic activity. Catalytic activity measurements were performed in 4 mL glass reaction vials. The reactors were heated in an oil bath placed on top of a magnetic stirrer. In a typical experiment, a stock solution consisting of either D-(-)-glucose (Sigma Aldrich) or D-(-)-fructose (Sigma Aldrich) was prepared, and 3 ml added to the reactor. The solvents used was deionised water and the sugar concentration was 100 mg/mL. After introducing the catalyst (10 mg or 40 mg), the reactor was closed and placed in the preheated oil bath at 140 °C for 3 h. The reaction was stopped by quenching the reaction vial at 0 °C in ice bath. The product mixture was analysed by a Shimadzu high performance liquid chromatography (HPLC) device equipped with a photo diode array (PDA) detector and an evaporative light scattering detector (ELSD) over a Biorad Aminex HPX-87P column. Glucose, fructose, and mannose were detected by the ELSD detector (ELSD) over a Biorad Aminex HPX-87P column. Glucose, fructose, and mannose were detected by the ELSD detector. Carbohydrates and HMF concentrations were calculated with respect to external standards. Recycle tests were performed using a 25 mL stainless steel reactor equipped with a PTFE inner lining (Berghof, BR-25). In a typical experiment, a stock solution consisting of 100 mg·mL⁻¹ D-glucose (Sigma Aldrich) in deionised water...
was prepared. 15 mL of solution was then added to the reactor along with 50 mg of catalyst. The reactor was then sealed and immersed into a preheated aluminium heating block on a magnetic stirring plate. After 3 h, the reaction was stopped by quenching the reactor at 0 °C in ice bath. The catalyst was filtered, washed with deionized water, and dried overnight at 80 °C. The recovered catalyst was used for the subsequent reaction cycle. The reactants and products were analysed by HPLC as above. The performances of catalysts were tested in a purpose-built flow reactor. For this, 80 mg of catalyst under study was pelletised and sieved to give a uniform particle size of 250 microns. The catalyst was then mixed with an inert material (silicon carbide) and loaded into the reactor resulting in a bed length of 8 cm. A 100 mg·L⁻¹ glucose solution in water was then pumped through the reactor at a constant flow rate whilst the reactor was heated to 140 °C. Activity of catalysts were tested at two different flow rates: 0.14 ml·min⁻¹ and 0.28 ml·min⁻¹. Liquid samples were collected at the exit of the reactor and the reactants and products were analysed by HPLC ex-situ as explained above.

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The UiO-66 metal organic framework has been demonstrated as a versatile solid-acid catalyst through decoration of its framework with numerous functional groups. These catalysts exhibit green, cheap, and scalable alternatives for biomass conversion.

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