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A hydrothermally stable ytterbium metal–organic framework as a bifunctional solid-acid catalyst for glucose conversion†

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$Yb_6(BDC)_7(OH)_4(H_2O)_4$ contains both bridging hydroxyls and metal-coordinated waters, possessing Brønsted and Lewis acid sites. The material crystallises from water at 200 °C. Using the solid as a heterogenous catalyst, glucose is converted into 5-hydroxymethylfurfural, *via* fructose, with a total selectivity of ~70% after 24 hours at 140 °C in water alone: the material is recyclable with no loss of crystallinity.

The conversion of biomass-derived glucose to organic molecules that may be used as precursors for the production of a variety of useful products for everyday life is important to provide sustainable production of chemicals. 5-Hydroxymethylfurfural (5-HMF) is one such organic molecule formed from glucose, *via* isomerisation to fructose as a common pathway, and is considered a platform molecule for the formation of a variety of useful chemicals ranging from plastics to drugs to fragrances and agrochemicals.[1] The two-step conversion of glucose requires both Lewis and Brønsted acid catalysis. Various studies have probed the possible pathways in solution when homogeneous, solution acids are used as catalysts in aqueous conditions,[2–6] and in ionic liquids.[7–13] Heterogeneous, solid-acid catalysts would, however, be desirable for this reaction if large-scale processes are to be developed,[14,15] avoiding significant amounts of mineral acids and metal salts, with easy of separation of the catalyst from the solution reagents. The use of zeolite-based catalysts that contain both Lewis and Brønsted acid sites has been studied and in particular tin-substituted zeolite beta (Sn-beta) has been shown as a particularly effective catalyst for the isomerisation of glucose into fructose in water,[16] or the direct formation of 5-HMF from glucose when a biphasic water/tetrahydrofuran reactor system is used.[17] Although Sn-beta is hydrothermally stable at low pH and the solid can be recycled, a significant disadvantage in its use, in particular on an industrial scale, is that the synthesis of the catalyst is a lengthy process requiring the use of seed crystals or a 40 day hydrothermal synthesis reaction using hydrofluoric acid, an extremely toxic and corrosive substance.[16] Furthermore, in continuous flow reactors Sn-beta can be unstable and is rapidly deactivated.[18]

Metal–organic frameworks have been considered as solid acid catalysts.[19] The dehydration of glucose to 5-HMF using MIL-101(Cr) functionalised with sulfonic acid groups (–SO$_3$H) was reported by Herbst and Janiak in 2016.[20] The highest 5-HMF yield of 29% was obtained at 130 °C with a 5 hour reaction time in tetrahydrofuran : water (39 : 1) mixture as solvent. Su *et al.* studied the same catalyst and found the highest conversions in mixed organic/aqueous solvent systems and demonstrated the effectiveness of the solid in a fixed-bed, continuous reactor.[21] MIL-101(Cr)–SO$_3$H showed high efficiency with more than 90% yield of 5-HMF when DMSO was used as solvent.[22] A composite of MIL-101(Cr) and chromium hydroxide showed optimum isomerisation of glucose into fructose in ethanol as solvent.[23] Other MOFs that have been used for glucose conversion include the zirconium-based NU-1000, with phosphate modification to induce Lewis acidity,[24] and the zirconium material UiO-66 with sulfonyl-modified ligands and inherent Lewis acidity from defects notably allowing conversion of glucose to fructose, along with a significant amount of 5-HMF in water alone,[25] or in alcohols as solvents.[26] While MIL-101 is constructed from the cheap and benign ligand benzene-1,4-dicarboxylate, the metal Cr is known to be toxic to humans and harmful to the environment; although these detrimental properties are largely associated with the +6 oxidation state, Cr^{3+} is considered an irritant, and its release into the environment is clearly undesirable if it were to encounter oxidising conditions.[27] Replacement of the chromium in MIL-101 by other trivalent cations leads to an instability of the material,[28] and we have therefore explored the chemistry of water-stable metal–organic frameworks containing more benign metals. Herein, we focus on materials that contain Yb^{3+} as the

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metal centre, with several reasons for the choice of this metal: (i) ytterbium triflate is well-known Lewis acid used for various organic transformations,[29] (ii) YbCl$_3$ in solution has already been used as a homogeneous Lewis acid catalysts for glucose conversion,[30,31] and (iii) metal–organic frameworks based on the rare-earth cations are known to be relatively chemically and thermally robust, as well as showing a wide structural variety.[32]

At least three different ytterbium MOFs crystallise from N,N-dimethylformamide (DMF)–water solutions of Yb^{3+} and benzene-1,4-dicarboxylic acid (H$_2$BDC), depending on the solvent composition and temperature.[33,34] This was the starting point for considering materials that might be water stable and thus the hydrated material Yb$_2$(BDC)$_3$(DMF)$_2$(H$_2$O)$_2$ (1) was selected, Fig. 1a, that crystallises from 50 : 50 DMF : water solutions at 100 °C[34] to investigate its behaviour in pure water. Hydrothermal treatment of (1) at 200 °C (ESI†) produced single crystals of Yb$_6$(BDC)$_7$(OH)$_4$(H$_2$O)$_4$ (2), whose structure, determined by single crystal X-ray diffraction was found to be analogous to yttrium and ytterbium materials reported by Weng *et al.*[35] The structure of (2) is completely different to (1). The latter, Fig. 1a contains dimers of 7-coordinate Yb^{3+} centres bridged the dicarboxylates, crosslinked by further BDC linkers to give α-Po type net that is interpenetrated with another such net, while (2) contains three distinct 8-coordinate Yb^{3+} centres bridged by hydroxides and BDC, two of which have terminal waters, with BDC ligands crosslinking denser regions of the structure, Fig. 1b. The building unit of the structure is a hexameric cluster, shown on Fig. 2, where six Yb centres are linked therein directly by shared oxygens. We also discovered that by moderating the synthesis conditions (see ESI†) the novel salt Yb$_2$(BDC)$_3$ (3) crystallised directly from water at 200 °C. The structure of (3) contains

isolated Yb centres, bridged by carboxylate functions of the BDC in a Z,Z-μ_2-η^1:η^1 mode, to give extended chains, BDC, Fig. 1c. The chains run in two perpendicular directions, to give a pseudo-layered structure, that are crosslinked by the bridging BDC ligands.

The synthesis of phase-pure (2), was subsequently achieved by addition of extra YbCl$_3$·6H$_2$O to provide the correct ratio of Yb : BDC as required by the chemical composition (see ESI†), Fig. 2. We also considered the possibility of inclusion of a Brønsted acid functionality by use of the sulfonic-acid modified 2-monosulfo-benzene-1,4-dicarboxylate (MSBDC) linker, using the sodium salt of the linker as precursor, as has found to be previously successful for modifying MOFs such as UiO-66 and MIL-101. This, however, yielded a novel crystalline structure only when DMF was used as solvent, [Yb(MSBDC)(DMF)$_2$] (4), and in this material the sulfonic acid functionality is deprotonated and coordinated to the Yb^{3+} centres, along with the carboxylate functionalities to yield a rather dense coordination polymer (ESI†). The material (4) was also found to be unstable under hydrothermal conditions, dissolving completely upon being heated in water above 100 °C.

The coordination polymers (2) and (3) both crystallise in water above 200 °C in 3 day synthesis reactions, so are extremely hydrothermally stable materials. For (2) the structure has channels containing occluded water, and thermogravimetric and thermodiffraction analysis reveals zeolitic behaviour with removal of water on heating to 200 °C (ESI†). Importantly, (2) has the potential for solid-acid properties with both bridging hydroxyls (Brønsted acidity) and coordinatively unsaturated Yb^{3+} once bound water is removed to lower the coordination number to seven (Lewis acidity), Fig. 2. In contrast (3) is a dense structure with fully saturated Yb centres, containing only the linker and the metal cation with no occluded species or additional ligands. We therefore chose (2) as a potential water-stable
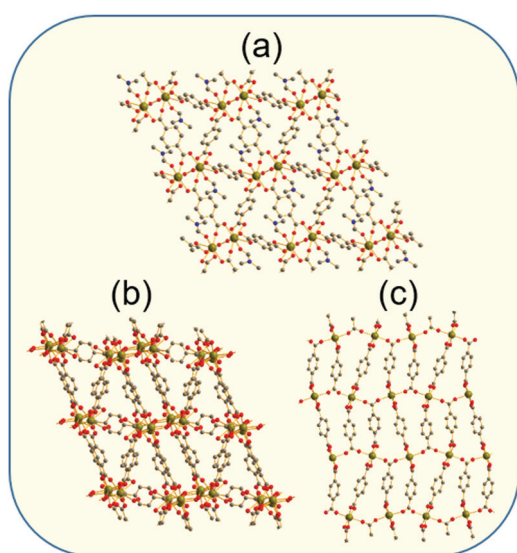

Fig. 1 The structures of (a) Yb$_2$(BDC)$_3$(DMF)$_2$(H$_2$O)$_2$ (1) viewed along *a*, showing one of the 3D connected networks of the interpenetrated structure, (b) Yb$_6$(BDC)$_7$(OH)$_4$(H$_2$O)$_4$ (2) along *b*, and (c) Yb$_2$(BDC)$_3$ (3) along *b*. The Yb atoms are olive, carbon grey, oxygen red and nitrogen blue. Hydrogen atoms are omitted for clarity and broken-off bonds represent the extended connectivity.
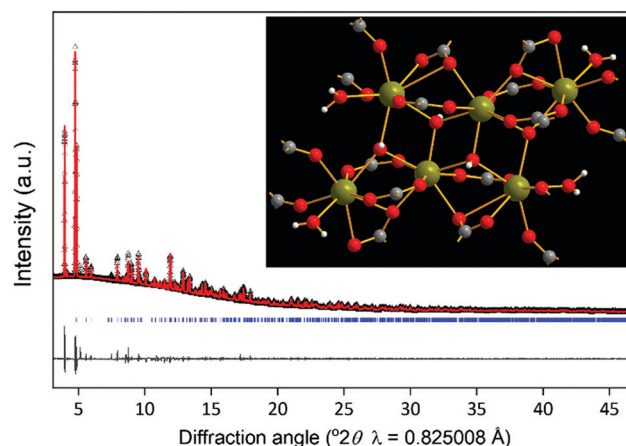

Fig. 2 Powder XRD Le Bail fit of a bulk sample of Yb$_6$(BDC)$_7$(OH)$_4$(H$_2$O)$_4$ (2) (see ESI† for crystal structure parameters). The data points are black triangles, the fitted pattern the red line, the difference curve the grey line and the blue ticks the positions of allowed Bragg peaks. The inset shows a view of the hexameric cluster unit in the material, with the same atom key as for Fig. 1, except for inclusion of hydrogen atoms as white spheres.

solid-acid catalyst, and examined the conversion of glucose in deionised water (pH = 7) at 140 °C, with the results summarised in Fig. 3 (see ESI† for full data). For comparison, we studied an aqueous solution of $YbCl_3$ as a homogeneous catalyst and Yb_2O_3 as a heterogeneous comparison (with the same total Yb content used for each). While the homogeneous solution of $YbCl_3$ gives the highest conversion of glucose, the selectivity towards fructose and 5-HMF is not high (48.3%); in fact previous work has shown that the pH needs to be lowered to obtain more significant conversion to the desired products from metal chloride salts, and then only at 170 °C using a biphasic solvent mixture.[30,31] Solid Yb_2O_3 shows a low conversion and only a small amount of fructose with no detectable 5-HMF in the product mixture after 3 hours, as expected in the absence of any Brønsted acid sites. In contrast (2) shows a reasonable conversion of glucose (~16%) after 3 hours and a selectivity towards fructose and 5-HMF of 50%. Since it may be expected that the kinetics of the heterogeneous reaction may be retarded compared to the homogeneous case, we examined long reactions. As can be seen on Fig. 3, extending the reaction time to 24 hours with (2), increases the conversion to a useful 28%, with a notable 65% selectivity towards 5-HMF, and 70% total selectivity towards fructose and 5-HMF. In all cases only negligible amounts of mannose are produced, a possible byproduct from the epimerisation of glucose.

The presence of acid sites in (2) was proven using ammonia temperature programmed desorption, which is consistent with the presence of two types of acid sites associated with the material, and pyridine adsorption that indicates both Brønsted and Lewis acid sites (ESI†). The fact that a significant amount of 5-HMF is produced, and that the proportion of this *vs.* fructose increases with extended reaction time, implies the presence of Brønsted acidity inherent to the material. Interestingly, lowering the pH to 2.5 with HCl offers no advantage: as shown on Fig. 3, the total conversion and distribution of products is similar to at pH = 7 at short reaction times, while after 24 hours the higher

conversion of glucose is associated with a much lower selectivity towards the desired products, suggesting decomposition of glucose by other pathways.

We examined the possibility of recycling the catalyst, and after recovering the solid, drying and adding to a fresh reaction, virtually the same conversions and selectivities were obtained over four runs, Fig. 4a. SEM shows little change in the particle morphology before and after use, with a distribution of crystallites micron-sized and less (Fig. 4b and c), while powder XRD, Fig. 4d, shows that the material remains intact after use as a catalyst, albeit contaminated with some amorphous humins as byproducts, consistent with the brown colour of the material after catalysis.

The ytterbium MOF (2) acts as a catalyst for glucose conversion in water alone, with no additional mineral acid necessary. The fact that significant amounts of 5-HMF are produced under these conditions, and is indeed the majority product after 24 hours, clearly indicates that the solid provides the necessary Brønsted acidity. Most other MOFs that have been reported so far have been studied in mixed water/organic solvents or with the addition of HCl (see Table S4, ESI†), but for the cases where just water has been used the ytterbium MOF outperforms the zirconium MOF NU-1000, which gave 60% conversion of glucose but yields of only 19% fructose and 2.3% 5-HMF (at 140 °C for 5 hours).[24] Sulfonyl-modified UiO-66 gave a similar 35.9% conversion to the Yb MOF in water alone and an initially high selectivity, but the efficiency dropped on recycling the solid.[25] Comparisons with other solid acids used for glucose shows that our materials offer significant advantages. For example, conventional solid-acid catalysts, such as sulfated zirconium oxide,[36] or sulfated niobium oxide,[37] require concentrated mineral acids, or other noxious reagents, for their synthesis. Tsapatsis and co-workers have recently shown that a composite of MIL-101(Cr) and $Cr(OH)_3$ gave high conversion of glucose but this was in a two-step process with ethanol as the solvent for isomerisation to ethyl fructoside, followed by addition of water to allow hydrolysis to fructose, each performed at 100 °C for 24 hours with almost 60% of the product fructose.[23] The use of multiple batch reaction steps requiring long reaction times is
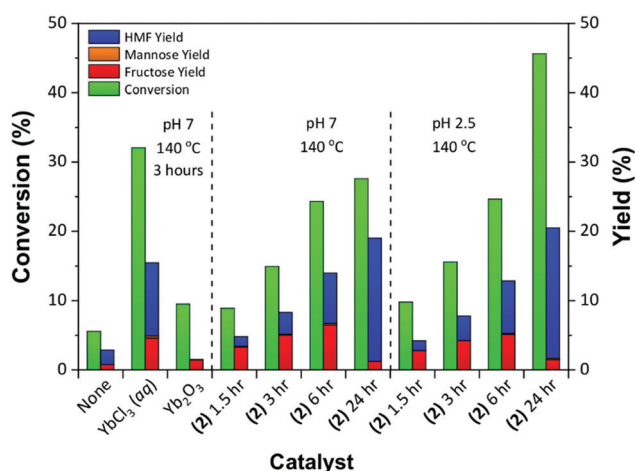

Fig. 3 Results of catalytic conversion of glucose using $[Yb_6(BDC)_7(OH)_4-(H_2O)_4]$ (2) and compared with a homogeneous solution of $YbCl_3$ and with solid Yb_2O_3.
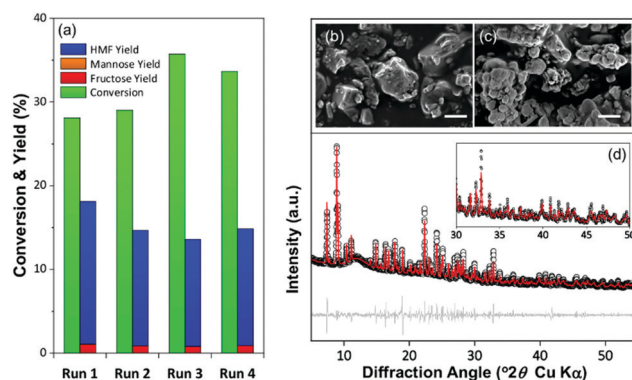

Fig. 4 (a) Recyclability of the catalyst (2) with SEM (b) before and (c) after heating in glucose at 140 °C for 24 hours (the scale bar is 1 μm) and (d) powder XRD (λ = 1.5406 Å) after reuse.

likely to be less attractive than continuous flow systems on scale-up. In fact, a lower conversion with higher selectivity may be useful if applied within continuous flow recycle reactors. Further work is needed to understand the molecular-scale mechanisms of the conversions of sugars over MOF catalysts: this includes the identity of intermediates and byproducts, and the possibility of disassembly of the surface of the MOF. This would then allow optimisation of activity and implementation of the materials in real processes. The use of hydrothermally stable materials containing the smaller lanthanide cations in heterogeneous solid-acid catalysis will also be of wider relevance to other industrial conversions, such as condensations and dehydrations, and applications where stability in water is needed,[38] for which metal–organic frameworks are only beginning to be being explored.[39,40]

Conflicts of interest

There are no conflicts to declare.

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