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Unexpected linker-dependent Brønsted acidity in the (Zr)UiO-66 Metal Organic Framework and application to biomass valorization

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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The catalytic activity of UiO-66 type Zr metal-organic frameworks can be tuned by the linker employed, e.g. nitro- or aminoterephthalic acid. Here we study composition-activity relations for the UiO-66 catalyzed dehydration of fructose into hydroxymethylfurfural, a carbon-neutral feedstock for chemicals and fuels. Variation of the substituents on the NO₂/NH₂ functionalized solids has a clear influence on the number of missing linkers around the Zr oxo clusters, on the hydrophobicity/hydrophilicity of the eventual metal-organic framework and on the Brønsted acidity. The thermally modulated UiO-66-NH₂ is able to yield 25 molecules of HMF per defective Zr site after 1h at 100°C, maintaining its activity in 4 consecutive runs.

Introduction

Of all metal-organic frameworks (MOFs) that have been studied in the past two decades, the robust, relatively inexpensive and non-toxic Zr-MOFs, such as UiO-66, have probably seen most applications as heterogeneous catalysts ^{1–3}. The high stability of UiO-66 is based on the high connectivity of its network and the robust nature of the Zr₆ building blocks, with each Zr₆ metal cluster being connected to maximally 12 benzene-1,4-dicarboxylate linkers ⁴. Moreover, its synthesis can nowadays be performed under scalable and green conditions, avoiding organic solvents and high temperatures ^{5–7}. Importantly, the real UiO-66 material may contain missing-linker defects and/or missing-cluster defects, as evidenced by thermogravimetric analysis, among other methods ^{8,9}. Since the presence of defects in the crystalline framework affects its physicochemical properties, e.g. porosity ¹⁰, proton conduction ¹¹ or even stability, different synthetic procedures have been proposed by our group and others, in order to increase or control the number of defects ^{12,13}. Among them, the thermal modulation approach is one of the simplest methods to increase the linker deficiency. The method consists in decreasing the synthesis temperature, which avoids the use of an excess of monocarboxylates or post-synthetic treatments (see Figure 1) ^{14,15}.

In depth studies have been devoted to the incorporation of Brønsted acid functional groups, e.g. -SO₃H¹⁶, and to the effects of

organic substituents on the Lewis acidity of the Zr sites in UiO-66 ¹⁷. Concerning Brønsted acidity, it was found that the hydroxyl group and water molecules which are coordinated to metal sites could work as Brønsted acid sites, as illustrated in Friedel-Craft alkylation of aromatics with MIL-69(C) as catalysts¹⁸. CO adsorption confirms the generation of Brønsted acidity on MIL-100(Cr) by grafting water to its framework¹⁹. Furthermore, a recent study demonstrates the Brønsted acidity of MIL-100(Cr/Fe) rising from the coordinated water at metal sites is crucial in the acetalization of aldehydes with alcohols, which shows a decreased net TON when coordinated water molecules are removed at high temperature²⁰. However, little attention has been devoted to the linker dependent Brønsted acidity of the highly polarizable Zr sites associated with missing linkers. Here we give a proof-of-concept that the acidity of the UiO-66-NO₂/NH₂ catalytic system can be tuned by the linker employed, BDC-NO₂ or BDC-NH₂ (BDC = benzene-1,4-dicarboxylate), in the model reaction of fructose dehydration to produce 5-hydroxymethylfurfural (HMF), a biobased platform molecule from which a variety of chemicals and fuels can be obtained ^{21–25}.

Figure 1. Structural defects and Brønsted acid sites (upon water coordination at Zr) generated by thermally modulated synthesis in UiO-66-NH₂. According to the literature, a near-perfect material is formed above 130 °C ¹⁴.

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Electronic Supplementary Information (ESI) available: details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Experimental

2.1 Materials

All chemicals are commercial and were used as received without further purification. ZrCl_4 (99.95%, ABCR), 2-aminoterephthalic acid ($\text{H}_2\text{BDC-NH}_2$, 99%, Acros Organics), 2-nitroterephthalic acid ($\text{H}_2\text{BDC-NO}_2$, 99%+, Acros Organics), DMF (Fisher Chemical), ethanol (Fisher Chemical), DMF (Acros Organics), $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (ABCR), H_3BTC (J&K, 99%), acetic acid (99.7%, Fisher Chemical), fructose (Sigma-Aldrich), 5-hydroxymethylfurfural (Sigma-Aldrich), DMSO-d_6 (Sigma-Aldrich), α -pinene oxide (Sigma-Aldrich), DCE (1,2-dichloroethane, Sigma-Aldrich), $\text{Cu}_3(\text{BTC})_2$ (Basolite, Sigma-Aldrich), Amberlyst® 15 hydrogen form (Sigma-Aldrich).

2.2 Characterization methods

Powder X-ray diffraction patterns (PXRD) were recorded on a Stoe STADI COMBI P diffractometer in high-throughput mode with monochromated $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$). Liquid ^1H NMR spectra of digested MOFs were collected on a Bruker AMX-300 spectrometer at 300 MHz for ^1H . MOF samples (20 mg) were digested in DMSO-d_6 (600 μL) with HF (30 μL) for liquid ^1H NMR.

Liquid ^1H NMR spectra of the fructose solution after reaction were collected on a Bruker AMX-400 spectrometer at 400 MHz for ^1H . Thermogravimetric analyses (TGA) were performed on a thermal analyzer NETZSCH STA 449 F3 Jupiter. Approximately 5 mg of sample was placed on an Al_2O_3 crucible which was heated at $5^\circ\text{C}/\text{min}$ under air atmosphere up to 650°C .

N_2 sorption isotherms were measured on a Micromeritics 3Flex Surface Analyzer at 77 K. Prior to analysis, all the MOFs were degassed for 5 h under vacuum at 150°C .

Water sorption isotherms were measured at 298 K on a Micromeritics 3Flex Surface Analyzer. Samples were activated at 150°C for 3 h under vacuum prior to analysis.

FTIR spectra were recorded on a Bruker Optics IFS 66V/S spectrometer (128 scans, 4 cm^{-1} resolution, $500\sim 4000 \text{ cm}^{-1}$) under vacuum. MOFs were pressed into wafers after dilution with KBr.

Solid-state NMR experiments were carried out on a 600 MHz Varian NMR system using 1.6 mm and 3.2 mm Varian CPMAS probes. Larmor frequencies for ^1H , ^2H , ^{13}C , and ^{15}N were 599.41 MHz, 92.01 MHz, 150.72 MHz and 60.76 MHz, respectively, and sample rotation frequency varied between 15 kHz and 40 kHz. ^1H - ^{13}C and ^1H - ^{15}N cross-polarization magic-angle spinning (CPMAS) measurements employed RAMP during CP block and high-power XiX heteronuclear decoupling during acquisition. CP-block duration and number of scans were 4 ms and 60 000 for ^1H - ^{13}C , and 1 ms and 180 000 for ^1H - ^{15}N CPMAS measurements. Repetition delay in these measurements was 1 s. The ^2H MAS spectrum was obtained by single-pulse excitation (pulse duration of 2.5 μs), whereas the T_2 -filtered ^2H MAS spectrum was obtained by using the Hahn echo sequence of pulses (delay between the pulses was 0.5 ms).

2.3 Experimental details

Synthesis of UiO-66 catalysts: According to literature,¹⁴ the temperature of the synthesis may affect the formation of defects. Therefore, this synthesis method is adapted from a previous report,¹⁵ because of the relatively low synthesis temperature and the high MOF yields obtained. A mixture of ZrCl_4 and linker was added to

DMF and sonicated until the solids were dissolved. Then the mixture was heated at 80°C for 24 h and next at 100°C for another 24 h in order to thermally modulate the generation of structural defects in the MOF. The MOF powder was collected by centrifugation, washed with DMF (3 times), ethanol (3 times) and dried at 150°C overnight.

Dehydration of fructose to HMF: In a typical catalytic test, 25 mg of fructose was dissolved in DMSO-d_6 (1 mL) and this solution was contacted with 10 mg of the MOF catalyst under stirring conditions at 100°C for 1 h. The products were analysed by HPLC using HMF standards as reference. The measurement was performed on an Agilent 1200 Series SL binary system equipped with a G1322A degasser, a G1312B binary pump, a G1367A automated sample injector, a G1316A thermostated column compartment, and a G1314A variable wavelength detector (VWD). HMF was separated on a ZORBAX XDB (250 mm) column, maintained at 40°C and detected by UV detection at $\lambda = 284 \text{ nm}$. The mobile phase consisted of acetic acid (0.1%) in Milli-Q water as aqueous phase and methanol as organic phase in a ratio of 10:90, with a flow rate of 0.6 mL/min and an injection volume of 2 μL . The amount of HMF was calculated according to the calibration curves obtained for the pure HMF solutions. ^1H NMR was also used to confirm the production of HMF: 9.55 (s, 1H, CHO), 7.50 (d, 1H, furan-CH), 6.61 (d, 1H, furan-CH), 4.51 (d, 2H, CH_2O) ppm.

Isomerization of α -pinene oxide: α -Pinene oxide (20 mg) was dissolved in dry 1,2-dichloroethane (DCE, 2 mL) with addition of the catalysts (20 mg). UiO-66- NH_2 was either directly used in catalysis without any activation or was activated at 150°C for 15 h. $\text{Cu}_3(\text{BTC})_2$ (20 mg) as a reference in this reaction was activated at 100°C for 20 h. Amberlyst® 15 (hydrogen form, 20 mg) was used as reference of Brønsted acid sites. The product was analyzed by GC-FID with a CP-Sil8 column.

Reuse study: Fructose (25 mg), UiO-66- NH_2 (10 mg) and DMSO-d_6 were added to a 10-mL glass vial. The reaction mixture was stirred for 1 h at 100°C . Then the solution and catalyst were separated by centrifugation. The solution was kept for HPLC measurement, while the catalyst was employed for the next catalytic reaction with fresh fructose solution, up to a total of four consecutive runs.

NH_3 Temperature-Programmed Desorption (TPD) Studies: Temperature programmed desorption was performed using a gas phase reactor setup with FTIR detector. Briefly, 108 mg of UiO-66- NH_2 was charged into a quartz tube between quartz wool plugs, and activated at 60°C for 3 h, or at 220°C for 2 h under N_2 flow (30 mL/min). Afterwards, the MOF was exposed to NH_3 (30 mL/min, 833 ppm) diluted by a N_2 flow (150 mL/min) at 100°C for 1 h. A N_2 flow (180 mL/min) was then used to flush away all physisorbed NH_3 during 1h. The desorption of NH_3 was carried out by increasing the temperature at $5^\circ\text{C}/\text{min}$ until 300°C .

Result and Discussion

First, five samples of mixed linker UiO-66, with different proportions of 2-aminoterephthalic acid ($\text{H}_2\text{BDC-NH}_2$) and 2-nitroterephthalic acid ($\text{H}_2\text{BDC-NO}_2$), were synthesized (see Table S1). Their XRD patterns suggest an identical topology for the mixed linker

UiO-66s as for the parent UiO-66 (see Figure 2a). The exact linker composition of the MOFs was determined by liquid ^1H -NMR analysis of the HF-digested samples in $\text{DMSO}-d_6$, showing the gradual increase of BDC- NH_2 together with the decrease of BDC- NO_2 (see Figure 2b). The linker composition was calculated based on the integration of the aromatic proton peaks at 7.4 and 8.4 ppm (for BDC- NH_2 and BDC- NO_2 , respectively) and the samples were labeled as UiO-66(NH_2) $_x$ (NO_2) $_{1-x}$, with $x = 0, 0.25, 0.49, 0.73$ and 1. The molar ratios of the synthesis mixtures are rather well reflected in those of the eventual materials (see Table S1). Moreover, the spectra of the digestion liquids show a peak at 8.1 ppm in the $-\text{NH}_2$ functionalized MOFs, indicating that the material contains formate ions, even though no formic acid was intentionally added during the synthesis. According to previous reports, formic acid can be formed by DMF hydrolysis during MOF synthesis²⁶. The ^1H -NMR spectra of the samples digested before and after activation at 220 °C show that the intensities of the formate and linker signals remained similar (Figure S1), while the physisorbed DMF was almost completely removed. This suggests that formic acid was incorporated in the MOF as a coordinated formate ion at the metal clusters, rather than as free, physisorbed formic acid. A reaction between formic acid and the amino groups of the linker during the MOF synthesis can be ruled out since no peaks corresponding to the formylated 2-aminoterephthalic acid are observed in the ^1H -NMR spectra²⁷.

The total number of linkers (BDC- NO_2 + BDC- NH_2) in the MOF samples was calculated from TGA analyses, according to previous reports (see supporting information for further details)²⁸. This value allows for an estimation of the number of Zr sites associated with defective positions (missing linkers) in the MOF crystal. Figure 2c shows the TGA curves of all MOFs under air atmosphere, which comprise three weight-loss stages. The initial weight loss starting from 40 °C to 130 °C is attributed to the physisorbed water present in the MOF, while the second weight loss occurring above 130 °C is due to the removal of occluded DMF and further dehydroxylation of the zirconium oxo-clusters. The last weight loss above 350 °C is due to the framework collapse upon the burning of the linker. Based on the TGA results, the linker deficiency (average coordination and defect concentration) was calculated as described in the literature²⁸ and listed in Table S2. None of the samples have their Zr_6 -cluster fully connected to 12 linkers, as previously reported by our group [17]. Instead, the linker deficiency increases in parallel with the amount of $-\text{NH}_2$ groups incorporated in the MOF. This is in line with the slightly lower thermal stability of the UiO-66- NH_2 in comparison to UiO-66- NO_2 (see Figure 2c).

N_2 physisorption (see Figure 2d) of the MOFs allows to calculate their BET surface area and pore volume, which are listed in Table S3. In our analysis, the experimental values obtained are slightly lower than the highest values previously reported for UiO-66- NH_2 and significantly lower than those for UiO-66- NO_2 ¹⁴. The fully amino-containing MOF, UiO-66- NH_2 , shows the highest BET area ($811 \text{ m}^2/\text{g}$), and a pore volume ($0.47 \text{ cm}^3/\text{g}$) significantly higher than for UiO-66- NO_2 ($422 \text{ m}^2/\text{g}$, $0.25 \text{ cm}^3/\text{g}$). Comparing these two samples, the 1.9 increase factor in surface area is due, at least partially, to the smaller steric volume of the amino groups, together with a higher number of

Figure 2. (a) PXRD patterns, (b) ^1H -NMR spectra in $\text{DMSO}-d_6$ after digestion with HF, (c) TGA curves under O_2 and (d) N_2 physisorption at 77K of UiO-66- $(\text{NH}_2)_x(\text{NO}_2)_{1-x}$ mixed-linker catalysts.

missing linkers which results in a more open framework in the case of the $-\text{NH}_2$ containing samples. Recently reported values of surface areas for UiO-66- NH_2 are ~ 1.5 times higher than those of UiO-66- NO_2 , showing how the surface area scales inversely to the substituent mass^{29,30}. In addition, UiO-66- NH_2 presents a larger amount of missing linkers or clusters, enhancing its microporosity. A UiO-66 sample was also prepared using the same synthesis method [14]. As expected, the porosity (BET area and pore volume) of this sample is higher than for both NH_2 and NO_2 functionalized ones (Figure S2), decreasing in the order UiO-66 > UiO-66- NH_2 > UiO-66- NO_2 . Moreover, judging from the pore size distributions (Figure S3a), large pores appear at $\sim 1.5 \text{ nm}$ for $-\text{NH}_2$ containing MOFs, indicating the fact that not only linkers but also clusters may be missing, which is consistent with the simulated calculation of UiO-66 with missing clusters by Bin Mu and co-workers³¹. This is confirmed by the low-angle ($2\theta = 1-10^\circ$) region (referred to as nanoregions) of the PXRD patterns of the MOFs, indicating a decrease of the reflection at 4° upon increasing nitro-linker content, suggesting the decrease of domains with reo topology (i.e. domains with ordered missing clusters) (see Figure S4).

The catalytic activity of these well-characterized, defective mixed-linker MOFs was evaluated in the dehydration of fructose, using DMSO as an environmentally acceptable solvent according to the CHEM21 classification³²⁻³⁴. Negligible HMF yield was produced in a control experiment of fructose dehydration in the absence of a catalyst, confirming the crucial role of the MOF as catalyst. With the increase of the number of $-\text{NH}_2$ groups in the MOF, the yield of HMF was improved from 47% (for pure UiO-66- NO_2) to 71% (for pure UiO-66- NH_2) after 1 h (see Figure 3a). According to the average coordination number from TGA results (Table S2), as the fraction of the NH_2 -linkers increases, there are more linkers missing, which leads to more Zr open sites that could play a role in the catalytic activity. Furthermore, the high BET area and pore volume of UiO-66- NH_2

Figure 3. (a) HMF yield from the dehydration of fructose over all UiO-66 MOFs; (b) ¹H NMR spectra of crude reaction mixture after fructose dehydration with UiO-66-NH₂ as catalyst. UiO-66-NH₂ was activated at 60 °C or 150 °C for 15 h. Solvent: DMSO-d₆, 400 MHz.

favor the access of fructose to the catalytically active sites (Figure S5).

In order to understand these results, it is important to consider the presence of water, and its remarkable effect on the activity of UiO-66-NH₂. When the latter material was activated at 150 °C for 15 h before being used, it completely lost its catalytic activity, and no HMF was formed at all (Figure 3b). However, when the material was only activated at 60 °C for 15 h, its activity was maintained, generating 71% HMF yield after 1 h. The effect of activation temperature on the HMF yield over UiO-66-NH₂ is displayed in Figure S7; the increase of activation temperature led to the gradual decrease of HMF yield till the loss of catalytic activity at 150 °C. This indicates that the presence of water, polarized by the Zr open coordination sites is directly related to the MOFs' Brønsted acidity, as has been reported in previous works^{35–37}. Proton conduction in UiO-66 has been reported to follow a Grotthuss mechanism via coordinated water at defective Zr sites^{11,38,39}. Such mechanism implies that a proton could hop between neighbouring water molecules and hydroxyl groups, either directly coordinated to the metal open sites or not^{11,38–43}. Logically, such mobile protons, and

Figure 4. (a) Acidity of the UiO-66-NH₂ before and after activation at 220 °C revealed by NH₃ temperature programmed desorption (TPD); (b) Evolution of physicochemical characteristics with NH₂-linker content in the MOF. (■) pH of an aqueous MOF suspension; (♦) average number of linkers surrounding each hexanuclear Zr cluster. pH values of the aqueous MOF suspensions were determined by dispersing 4 mg of MOF in 20 ml of MQ water and equilibrating for 120 min. The dash blue line is a guide for the eye. The coordination number of the Zr clusters was determined by TGA (see Figure 2c).

the Brønsted acidity associated with them, are only available if the material is in the hydrated state.

To confirm that water on UiO-66-NH₂ gives rise to Brønsted acidity, NH₃ temperature programmed desorption (NH₃-TPD) was performed^{38,44}. NH₃, as a Brønsted base, is expected to interact primarily with Brønsted acid sites, and much less with the hard Lewis acid sites on Zr⁴⁺, if these are available. In the defective, hydrated UiO-66-NH₂, the NH₃ probe can interact not only with the four μ₃-OH groups of each cluster, but also with the coordinated water (Zr-H₂O) and hydroxide group (Zr-OH) at the open coordination sites formed by the missing linkers. This results in a large area under the NH₃-TPD curve (see Figure 4a). On the other hand, in the dehydrated UiO-66-NH₂ sample, thermally treated at 220 °C, the NH₃ can only interact with the μ₃-OH groups, and the amount of adsorbed NH₃ severely decreases. Moreover, as depicted in Figure 4a, after activation at 220 °C, the interaction of NH₃ with the surface becomes much weaker, as

shown by the lower temperature of the maximum in the desorption profile (150 °C vs. 177 °C). This clearly indicates that the loss of water upon thermal activation decreases the MOF's Brønsted acidity.

Another clear indicator for the acidity of the hydrated materials is the pH measured when they are suspended in water (Figure 4b). As the fraction of -NH₂ functionalized linkers increases, the suspension's pH decreases. Figure 4b shows that this trend is paralleled by a decrease of the number of linkers around the Zr₆O₄(OH)₄ clusters. This confirms that the acidity is generated on the Zr defect sites created by missing linkers, which are most abundant in the purely -NH₂ functionalized material.

Test reactions were also carried out to identify the nature of the acid sites (Brønsted or Lewis type) on the hydrated vs. dehydrated materials. The isomerization of α -pinene oxide to form campholenic aldehyde is known to be catalyzed by Lewis acid sites with a selectivity as high as 85%, while using Brønsted acid sites the selectivity is usually lower than 50%⁴⁵. The results for UiO-66-NH₂ are listed in Figure S8. The Lewis acidic Cu₃(BTC)₂ MOF and Brønsted acidic Amberlyst-15 resin with -SO₃H groups were applied as references for this reaction. The campholenic aldehyde selectivity of Cu₃(BTC)₂ amounted to 91%, while that of Amberlyst-15 was only 29%. The UiO-66-NH₂ sample after dehydration at 150 °C displayed a higher selectivity (54%) than the hydrated one (11%), which directly relates the coordinated water in the hydrated Zr MOF to its Brønsted acidity.

Additional characterization of the five differently substituted materials was pursued by FTIR spectroscopy (see Figure 5a and b). At room temperature, the water confined in the pores of the non-thermally treated samples gives rise to a broad peak of ν_{O-H} stretching vibrations (~ 3400 cm⁻¹)^{46,47}. For UiO-66-NH₂, the intensity of this peak is much larger than for UiO-66-NO₂. There are two reasons for this: first, the broad ν_{O-H} band of water (3600-3200 cm⁻¹) overlaps with the symmetric and asymmetric stretching ν_{N-H} vibrations of the NH₂ group. Secondly, UiO-66-NH₂ could be expected to be more hydrophilic (cfr. infra), because of the presence of the defect Zr sites, and because of the H-bond donating properties of the -NH₂ groups. After the thermal treatment at 150 °C, the physisorbed water is largely removed, and the ν_{O-H} vibrations of the Zr₆O₄(OH)₄ cornerstone can be clearly discerned, with two peaks clearly

differentiated at 3672 and 3634 cm⁻¹. As discussed by Shearer et al.⁴⁸, the observation of different ν_{O-H} peaks, even before the thermal dehydroxylation of the cluster sets in, could find its origin in linkers missing around the cluster, giving rise to variations in the local symmetry.

Further information on the Brønsted acidity in the hydrated UiO-66-NH₂ was gathered through solid state NMR. ¹H-¹³C CPMAS and ¹H MAS NMR spectra of the hydrated and dehydrated UiO-66-NH₂ are shown in Figure 6. For the dehydrated UiO-66-NH₂, all ¹³C and most ¹H signals are readily assigned based on chemical shift prediction (see Table S4), and based on a previously reported 2D ¹H-¹³C LG-HETCOR measurement⁴⁹; assignments are shown in Figure 6. In the spectrum of the hydrated UiO-66-NH₂, most of ¹³C signals correspond closely to those of the dehydrated material, giving similarly sharp peaks, with the exception of the C5 signal at 150 ppm. This signal, corresponding to the C atom to which the -NH₂ group is attached, is significantly broadened and extended towards smaller chemical shift values. According to chemical shift predictions, a decrease of the chemical shift could be indicative of strong hydrogen bonding to the -NH₂ group, or even of a protonation that would give rise to NH₃⁺. However, in the latter case, a decrease of ~ 10 ppm could be expected for the C5 ¹³C signal, while the spectrum shows that the upfield displacement is much more limited. As the most plausible explanation, we therefore propose a strong hydrogen bonding to the -NH₂ group in the hydrated material.

The analysis of the ¹H MAS NMR data is consistent with that of the ¹H-¹³C CP-MAS spectra. In the dehydrated material the -NH₂ protons resonate at a shift of ~ 5.5 ppm, whereas in the hydrated material, the signal of these protons moves to 6.9 ppm, as expected for a -NH₂ group that interacts with acidic protons. To confirm that the protons at 6.9 ppm belong to the -NH₂ group, the material was dehydrated, and subsequently rehydrated using D₂O (Figure S10). The ²H MAS NMR spectrum shows that the most efficient exchange between the protons and deuterons is for the nuclei that resonate at ~ 6.9 ppm, confirming the assignment to hydrogen bonded -ND₂ (or NHD).

Finally, a clear evidence for an acidic proton interacting with the -NH₂ group comes from the ¹H-¹⁵N CPMAS NMR measurements (Figure 6). The ¹⁵N NMR signal of the hydrated material is by ~ 10 ppm displaced from the ¹⁵N NMR signal of the dehydrated material (from

Figure 5. (a) Normalized FTIR spectra of the UiO-66-NH₂/NO₂ samples at room temperature and (b) thermally treated at 150 °C.

Figure 6. (a) ^1H - ^{13}C CPMAS NMR spectrum, (b) ^1H MAS NMR spectrum and (c) ^1H - ^{15}N CPMAS NMR spectrum of the hydrated (blue) and dehydrated (black) UiO-66-NH₂.

-314 to -323 ppm).

Overall, much evidence supports that UiO-66-NH₂ is a more suitable Brønsted acid catalyst than UiO-66-NO₂ because of the larger number of defect sites at Zr, and because of the larger porosity. An additional beneficial factor may be the material's hydrophilicity, because of the large number of polar amino groups⁵⁰. This characteristic was quantified by measuring the water adsorption isotherms. Figure S11 shows that UiO-66-NH₂ could immediately capture water at low P/P_0 (< 0.005) while on UiO-66-NO₂ water uptake was low until a P/P_0 value of 0.024 was reached. In addition, the maximum water uptake of UiO-66-NH₂ was larger than for UiO-66-NO₂, which is related to the former's higher porosity⁵¹. The ability of -NH₂ groups to form hydrogen bonds with water molecules results in an enhanced water concentration around the Zr clusters.

The reusability of UiO-66-NH₂ was investigated by replacing the fructose solution, after 1 h reaction, in four additional consecutive runs (Figure 7). A slight drop of approximately 7% of the yield of HMF in every run was observed, even though the overall catalytic activity was rather well preserved over four runs. The slight drop could be attributed to the deposition of organic compounds in the MOF's pores, such as humins as unwanted polymeric side products. This was confirmed by the decrease of BET area to 754 m²/g as is illustrated in Figure S12. The MOF shows a cumulative TON(Zr) after four reaction cycles of 9 molecules of HMF converted per Zr atom in the UiO-66-NH₂. However, since the Zr sites are still for a majority coordinated with linkers (7.5 linkers per Zr₆ cluster), the catalytic activity of the unsaturated Zr sites increases up to a TON of 25 molecules of HMF produced per defective Zr site. The PXRD pattern of UiO-66-NH₂ after 4 runs (Figure S13) was identical to the original one, indicating its stability under these reaction conditions. Moreover, ICP analysis of the reaction solution shows that less than 1wt % Zr amount leached from the solid.

Figure 7. Reusability of UiO-66-NH₂ under the following reaction conditions: fructose (25 mg), DMSO-d₆ (1 mL), MOF (10 mg), 100 °C, 1h.

Conclusion

In conclusion, the high catalytic activity of UiO-66-NH₂ for the fructose dehydration to form HMF was studied in detail. Comparison with materials containing the NO₂-functionalized linker learns that numerous Brønsted acid sites are available in the hydrated UiO-66-NH₂ because of a high number of missing linkers. The water contained in the pores enhances the activity of the MOF catalyst, due to the favored formation of solvated protons associated to Zr defective sites. This results in a larger number of Brønsted acid sites. The UiO-66-NH₂ material was as well studied by a series of characterization techniques such as multinuclear NMR, N₂ and H₂O physisorption, TGA, pH measurements etc. This shows that additional factors favoring the high activity of hydrated UiO-66-NH₂ are the large available pore volume and the hydrophilicity of the material. Per open Zr site, up to 25 molecules of HMF are produced

per run, and the material maintains significant activity over consecutive runs.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

G. Fu thanks the CSC for fellowships, grant number: 201406230044. DDV thanks FWO (G.0D0518N) and KULeuven (Metusalem) for research project funding. We thank Prof. I. Vankelecom and C. Van Goethem for providing the TEM measurements.

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