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# Direct Synthesis of Hierarchically Porous Metal–Organic Frameworks with High Stability and Strong Brønsted Acidity: The Decisive Role of Hafnium in Efficient and Selective Fructose Dehydration

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## Supporting Information

**ABSTRACT:** The direct synthesis of metal–organic frameworks (MOFs) with strong Brønsted acidity is challenging because the functional groups exhibiting Brønsted acidity (e.g., sulfonic acid groups) often jeopardize the framework integrity. Herein, we report the direct synthesis of two hierarchically porous MOFs named NUS-6 composed of either zirconium (Zr) or hafnium (Hf) clusters with high stability and strong Brønsted acidity. Via the modulated hydrothermal (MHT) synthesis, these two MOFs can be easily synthesized at a low temperature (80 °C) with high throughput. They exhibit BET surface areas of 550 and 530 m<sup>2</sup> g<sup>-1</sup> for Zr and Hf one, respectively, and a unique hierarchically porous structure of



coexisting micropores (~0.5, ~0.7, and ~1.4 nm) and mesopores (~4.0 nm) with dangling sulfonic acid groups. Structural analysis reveals that the hierarchical porosity of NUS-6 is a result of missing linkers and clusters of the parental UiO-66 framework. These unique features make NUS-6 highly efficient and selective solid acid catalysts for dehydration of fructose to 5-hydroxymethylfurfural (HMF), in which NUS-6(Hf) demonstrates a superior performance versus that of NUS-6(Zr) because of the stronger Brønsted acidity contributed from Hf- $\mu_3$ -OH groups as well as smaller pore sizes suitable for the restriction of unwanted side reactions. Our results have demonstrated for the first time the unique attributes of Hf-MOFs featured by superior stability and Brønsted acidity that can be applied as heterogeneous catalysts in biobased chemical synthesis.

## INTRODUCTION

Metal–organic frameworks (MOFs) as emerging porous crystalline materials consisting of metal ions/clusters and organic ligands have demonstrated strong potential as heterogeneous catalysts.<sup>1–6</sup> The first example of MOFs as Lewis acid catalysts (unsaturated metal sites) was reported for the cyanosilylation reaction of aldehydes.<sup>7</sup> Since then, numerous MOFs have been used as Lewis acid catalysts for various reactions, such as cyanosilylation,<sup>8–11</sup> ring opening reaction,<sup>11,12</sup> Mukaiyama-Aldol reaction,<sup>9</sup> Knoevenagel condensation,<sup>13,14</sup> redox reaction,<sup>15–18</sup> Pechmann reaction,<sup>19</sup> CO<sub>2</sub> fixation,<sup>20</sup> dehydrogenation,<sup>21</sup> etc. Compared to the relatively comprehensive work that has been conducted on the Lewis acidity of MOFs, exploring Brønsted acidity of MOFs is more challenging and remains less explored,<sup>22,23</sup> mainly because of the weakened framework stability caused by the introduction of Brønsted acidity typically through sulfonic acid groups.<sup>24,25</sup>

Therefore, most researchers adopted the postsynthetic modification  $(PSM)^{26}$  route to introduce sulfonic acid groups into MOFs for applications such as heterogeneous catalysis<sup>27</sup> and proton conductivity.<sup>28,29</sup> However, the controlled sulfonation, compromised crystallinity, and restrained catalytic efficiency remain the major issues to be further resolved. Direct synthesis of sulfonated MOFs may solve most of the issues mentioned above but relies largely on the superior stability of the MOF scaffolds. One of the very few successful examples is the Cr-based MOF MIL-101-SO<sub>3</sub>H, which was directly synthesized from sulfonated ligand [monosodium 2-sulfoterephthalic acid (BDC-SO<sub>3</sub>Na)] and was applied as an efficient solid acid catalyst in cellulose hydrolysis<sup>30</sup> and

Received: January 12, 2016 Revised: March 25, 2016 esterification of *n*-butanol.<sup>31</sup> However, the stringent synthetic conditions and toxic inorganic reagents of Cr MOFs greatly limit their applications.

Zr MOFs such as UiO-66 have received a great deal of attention because of their facile synthesis, high chemical stability, and wide choice of ligands.<sup>32,33</sup> Foo et al. initially attempted the direct solvothermal synthesis of sulfonated UiO-66 (UiO-66-SO<sub>3</sub>H), which however collapsed upon activation and was attributed to the anionic charge or protons from the sulfonate groups interacting with the 12-connected Zr<sub>6</sub> clusters.<sup>34</sup> A modified solvothermal synthesis was adopted by Biswas et al. in synthesizing a more stable UiO-66-SO<sub>3</sub>H that survived after activation with a Langmuir surface area of 769 m<sup>2</sup>  $g^{-1.35}$  The increased stability was attributed to different synthetic conditions as well as different guest molecules encapsulated within the pores. Juan-Alcañiz et al. used BDC-SO<sub>3</sub>K to synthesize sulfonated UiO-66 with pure water as the solvent, affording HSO3-Zr-MOF with a new framework topology containing 8-connected Zr<sub>6</sub> clusters that is different from the UiO-66 type topology.<sup>31</sup> This MOF exhibited high activity and full reusability in the esterification of *n*-butanol with acetic acid, but with limited thermal stability. Recently, Taylor et al. modified the hydrothermal synthesis of HSO<sub>3</sub>-Zr-MOF by using BDC-SO<sub>3</sub>H as the ligand with various amounts of acids (acetic acid or sulfoacetic acid) as additives.<sup>36</sup> The fully determined crystal structure of this MOF revealed a combination of micropores and mesopores in this framework caused by missing ligands and Zr clusters. However, this MOF also suffered from limited thermal stability and started to decompose upon activation at higher temperatures ( $\geq$ 70 °C).

Besides organic ligands, the inorganic metal clusters of MOFs might be another source of intrinsic Brønsted acidity. Belonging to the same elemental group, Hf and Zr share similar properties. Therefore, Hf MOFs should possess equally high thermal and chemical stability, which has been proven previously.<sup>37</sup> In addition, the higher dissociation energy of the Hf–O bond (802 kJ mol<sup>-1</sup>) versus that of the Zr–O bond (776 kJ mol<sup>-1</sup>) could possibly turn the  $\mu_3$ -OH groups of Hf clusters into Brønsted acid sites, as suggested by Beyzavi et al.<sup>2</sup> Therefore, sulfonated Hf MOFs containing both organic and inorganic Brønsted acid sites should be excellent solid acid catalysts, which however have not been reported so far. In our previous studies, we have reported a modulated hydrothermal (MHT) approach that can be used to synthesize a series of highly stable Zr and Hf MOFs in a green and scalable way.<sup>33,38,39</sup> In this study, the MHT approach is used to prepare two sulfonated and hierarchically porous MOFs containing Zr and Hf clusters, respectively. By acid-base titration, we have for the first time proven the Brønsted acidity of Hf MOFs is stronger than that of Zr MOFs. In addition, the Hf MOFs exhibited catalytic performance better than that of their Zr counterparts in catalyzing the dehydration of fructose to 5hydroxymethylfurfural (HMF).

## RESULTS AND DISCUSSION

Powder crystalline MOF products named NUS-6 were easily obtained by a typical MHT process in which mixtures of BDC- $SO_3Na$  with either  $ZrCl_4$  or  $HfCl_4$  were mildly heated at 80 °C in aqueous solutions with the addition of acetic acid as the modulator (see the Supporting Information for details). Rietveld refinements of the synchrotron powder X-ray diffraction (PXRD) data (Figure 1) of both NUS-6(Zr) and NUS-6(Hf) reveal isostructures identical to the one reported by



Figure 1. Rietveld refinements of (a) NUS-6(Zr) and (b) NUS-6(Hf) based on synchrotron PXRD data.

Taylor et al.,<sup>36</sup> but with slightly different unit cell sizes (Table S1). Taking NUS-6(Hf), for example, we can best describe this crystal structure by partially replacing the 12-connected Hf<sub>6</sub> clusters in the parental UiO-66 type framework (Figure 2a) with 9-connected Hf<sub>6</sub> clusters yielding periodic missing of ligands and Hf<sub>6</sub> clusters (Figure 2b). As a result, squashed mesopores ( $\sim 2.6$  nm  $\times$  3.6 nm, measured from Hf to Hf vertexes) that are interconnected with microporous tetrahedral and octahedral cavities from UiO-66 type topology affording a hierarchical porous structure can be generated (Figure 2c). Such a hierarchically porous structure should be highly beneficial for heterogeneous catalysis because of the dense catalytic sites packed in micropores and facile mass transfer through mesopores, as has been suggested in MOFs and zeolites.<sup>11,40,41</sup> On the basis of the isostructural analysis of the calculated crystal model, a molecular formula of  $C_{120}O_{291}S_{15}Zr_{21}H_{386} \{ [Zr_6O_4(OH)_8L]_{3.5} \cdot xH_2O, MW = 8873,$ Zr/S molar ratio of 1.40} was further obtained for NUS-6 (Zr), while NUS-6 (Hf) shared an identical formula with Zr being replaced by Hf (Table S1).

Besides the structural features mentioned above, the rich and versatile acid sites also make NUS-6, especially NUS-6(Hf), attractive as heterogeneous catalysts. As revealed by one fragment of the NUS-6(Hf) framework containing one 12-

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**Figure 2.** (a) A 12-connected  $Hf_6$  cluster. (b) A 9-connected  $Hf_6$  cluster. (c) A 2 × 2 × 2 super unit cell of UiO-66(Hf) with *a* = 20.7006(3) Å. (d) A single unit cell of NUS-6(Hf) with *a* = 41.4718(2) Å. (e) A 1 × 2 × 2 super unit cell of NUS-6(Hf) with mesopores indicated by yellow spheres. (f) A fragment of NUS-6(Hf) with potential Brønsted acid sites labeled by red clouds and Lewis acid sites labeled by cyan clouds.

connected Hf<sub>6</sub> cluster and one 9-connected Hf<sub>6</sub> cluster linked by one sulfonated ligand (Figure 2f), two sources of Brønsted acidity can be identified, one from the sulfonated ligand and the other from  $\mu_3$ -OH groups of Hf clusters. In addition, the coordinatively unsaturated Hf sites in the 9-connected Hf<sub>6</sub> cluster may potentially serve as Lewis acid sites. Compared to NUS-6(Hf), NUS-6(Zr) may lack the source of Brønsted acidity from Zr<sub>6</sub> clusters, but with a possibly stronger Lewis acidity from the coordinatively unsaturated Zr sites due to its smaller cation radius.<sup>42</sup> These features make NUS-6 very special solid acids containing both Brønsted acidity and Lewis acidity that have rarely been reported in MOFs.<sup>43</sup>

The presence and distribution of sulfonate groups in NUS-6 are confirmed by Fourier transform infrared spectroscopy (FTIR) (Figure S1) and energy-dispersive X-ray spectroscopy (EDS) (Figures S2 and S3). The characteristic FTIR peaks at 1230 and 1180 cm<sup>-1</sup> can be attributed to the symmetric and asymmetric stretching of O=S=O, respectively.<sup>28</sup> Because of the strong acidic reaction conditions, the ligand BDC-SO<sub>3</sub>Na is fully protonated in situ into BDC-SO<sub>3</sub>H in NUS-6 as revealed by the missing Na signal from EDS elemental mapping (Figures S2 and S3). This finding is in agreement with previous studies in which BDC-SO<sub>3</sub>Na or BDC-SO<sub>3</sub>K was also protonated in situ when used for the growth of MOFs under acidic synthetic conditions.<sup>31,34</sup> The field-emission scanning electron microscopy (FE-SEM) images (Figure 3a,b) show that both NUS-6(Zr) and NUS-6(Hf) crystals have a highly symmetric polyhedral morphology, which is rarely seen in our previous studies of Zr MOFs obtained through the MHT approach.<sup>33,38</sup> Closer observation of these crystals reveals agglomerations of small particles (Figure 3a,b, insets), suggesting a reversed crystal growth mechanism in which starting materials (ligands and metal salts) form disordered aggregates that undergo recrystallization from surface to core.<sup>44</sup> The crystal growth process of NUS-6(Zr) was further monitored by PXRD (Figure S4), FE-SEM (Figure S5), and dynamic light scattering (DLS) (Figure S6), confirming the formation of amorphous nanoparticles at first, which agglomerated and grew into crystalline particles matching well with the aforementioned reversed



**Figure 3.** FE-SEM images of (a) NUS-6(Zr) and (b) NUS-6(Hf) (scale bars represent 1  $\mu$ m; inset scale bars represent 100 nm) and HR-TEM images of (c) NUS-6(Zr) and (d) NUS-6(Hf) (scale bars represent 2 nm).

crystal growth mechanism.<sup>44</sup> The internal fine structures of NUS-6 crystals were investigated by high-resolution transmission electron microscopy (HR-TEM) (Figure 3c,d), where highly crystalline domains can be found with lattice spacings of  $\sim 0.29$  nm representing the (110) crystal plane of NUS-6 MOFs. These crystalline domains have a small size ( $\sim 5$  nm) and are distributed randomly within the crystal, suggesting an agglomeration of crystalline subparticles within one big quasicrystal that also proves the suggested crystal growth mechanism. It is probably the amphiphilicity of ligand and aqueous reaction media that leads to fast nucleation. However, the detailed crystal growth mechanism remains to be further studied.

Stability is another important factor in evaluating sulfonated MOFs as heterogeneous catalysts. The previously reported sulfonated Zr MOFs are more or less limited by their low thermal stabilities: the frameworks start to decompose upon activation at higher temperatures.<sup>31,34–36</sup> To test the stability of NUS-6 MOFs, the samples were vigorously activated by solvent exchange for 3 days and evacuation under a dynamic vacuum at 150 °C for 24 h to fully remove trapped guest and solvent molecules such as ligand, water, acetic acid, etc. To our surprise, both NUS-6(Zr) and NUS-6(Hf) can survive under such harsh activation conditions, which is proven by almost unchanged PXRD patterns (Figure 5) and hybrid type I/IV N<sub>2</sub> sorption isotherms at 77 K with mild hystereses between adsorption and desorption branches (Figure 4a), indicating hierarchical micro/



**Figure 4.** (a)  $N_2$  sorption isotherms at 77 K of NUS-6 MOFs with the inset featuring adsorption–desorption hystereses. (b) Pore size distribution of NUS-6 MOFs calculated by NLDFT and BJH models (inset).

mesoporous textures that are in accordance with the crystal structures. NUS-6(Zr) has a Brunauer–Emmett–Teller (BET) surface area of 550 m<sup>2</sup> g<sup>-1</sup>, which is lower than the value of 1187 m<sup>2</sup> g<sup>-1</sup> reported by Taylor et al., indicating either partial framework collapse or the existence of nonporous impurities.<sup>36</sup> Compared to NUS-6(Zr), NUS-6(Hf) has a relatively lower BET surface area of 530 m<sup>2</sup> g<sup>-1</sup>, probably because of the introduction of heavier Hf cations.<sup>45</sup> The pore size distribution of NUS-6 calculated using nonlocal density functional theory (NLDFT) reveals three distinct pore sizes of ~6, ~8, and ~12

Å (Figure 4b). NUS-6(Hf) has a pore size of ~5.5 Å that is slightly smaller than that of NUS-6(Zr) (~6 Å), possibly because of the larger radius of Hf that helps to reduce the pore size. Interestingly, the pore size distribution calculated using the Barrett–Joyner–Halenda (BJH) model suggests the existence of mesopores with sizes of ~3.8 and ~4.2 nm for NUS-6(Zr) and NUS-6(Hf), respectively (Figure 4b). Such mesopores may come from either missing ligands/clusters revealed by the crystal structures or the interstitial voids of crystalline subparticles constituting the NUS-6 quasi-crystals.<sup>38</sup>

Compared to the previously synthesized sulfonated Zr MOFs,  $^{31,34-36}$  there are mainly three distinctions in our synthetic procedure. (1) BDC-SO<sub>3</sub>Na is directly used as the ligand without preprotonation. (2) Water is used as the solvent with the addition of acetic acid as the modulator using a different ratio. (3) The reaction is conducted at a lower temperature of 80  $^\circ$ C, which actually is the lowest temperature reported so far for the synthesis of Zr or Hf MOFs.<sup>33</sup> We suspect it is the amphiphilic ligand and mild reaction condition that lead to molecular-level self-assembly of reagents accounting for the reversed crystal growth. As a result, NUS-6 quasi-crystals containing crystalline subparticles, which may prevent the framework from collapsing under harsh activation conditions due to the milder capillary force experienced by each subparticle, are formed.<sup>46</sup> To fully evaluate the stability of NUS-6 MOFs, PXRD and  $N_2$  sorption tests were performed on a series of samples under various conditions (Figure 5 and Figure



Figure 5. PXRD patterns of NUS-6 MOFs under various conditions.

S7). Both NUS-6(Zr) and NUS-6(Hf) can survive under acidic conditions (pH 1) without major changes in PXRD and  $N_2$  uptake. However, their stability under basic conditions is very poor as shown by the almost completely amorphous structures after exposure to basic solutions (pH 12). The different stability of NUS-6 under acidic versus basic conditions is identical to those of other reported Zr MOFs such as UiO-66.<sup>47</sup> The long-term stability test of NUS-6 was performed by exposing the samples to air for 10 months. Although there is no noticeable change in the PXRD patterns, NUS-6(Zr) exhibits a partial degradation as revealed by the reduced rate of  $N_2$  uptake, while NUS-6(Hf) remains less affected (Figure S7). The superior stability of NUS-6(Hf) versus that of NUS-6(Zr) can be explained by the dissociation energy of the Hf–O bond (802 kJ mol<sup>-1</sup>) being higher than that of the Zr–O bond (776 kJ

 $mol^{-1}$ ), which is also confirmed by thermogravimetric analysis (TGA) (Figure S8) in which NUS-6(Hf) exhibits a less obvious weight loss (5.65%) compared to that of NUS-6(Zr) (17.88%) in the temperature range of 200–400 °C. These results confirm the excellent stability of NUS-6, especially NUS-6(Hf), which grants their application in various fields such as gas separation and heterogeneous catalysis.

Anthropogenic CO<sub>2</sub> emissions have aroused worldwide concern,<sup>48</sup> and MOFs have been proposed as promising adsorbents for postcombustion CO<sub>2</sub> capture, in which CO<sub>2</sub> needs to be separated from flue gas containing mainly N<sub>2</sub> (~75%) and CO<sub>2</sub> (~15%) saturated with moisture.<sup>49</sup> The ideal adsorbents for this operation should have the features of high CO<sub>2</sub> working capacity (CO<sub>2</sub> uptake at 0.15 bar and 298 K), good CO<sub>2</sub>/N<sub>2</sub> selectivity, excellent water stability, and low water interference. NUS-6 MOFs were systematically evaluated for this application. NUS-6(Hf) has a CO<sub>2</sub> working capacity (0.30 mmol g<sup>-1</sup>) slightly higher than that of NUS-6(Zr) (0.29 mmol g<sup>-1</sup>) (Figure 6a), but the former has a smaller BET



Figure 6. (a)  $CO_2$  and  $N_2$  uptake of NUS-6 MOFs at 298 K. (b)  $Q_{st}$  of  $CO_2$  in NUS-6 MOFs. (c) IAST  $CO_2/N_2$  selectivity of NUS-6 MOFs. (d) Water vapor uptake of NUS-6 MOFs at 273 K.

surface area. This is probably because of the smaller pore size of NUS-6(Hf) as well as the polarized  $\mu_3$ -OH groups of Hf clusters, which strengthen the interactions between  $CO_2$  and MOFs.<sup>45,50</sup> Such strengthened  $CO_2$ -MOF interactions are quantified by the isosteric heat of adsorption  $(Q_{st})$  of CO<sub>2</sub> (Figure 6b), whereas the zero-coverage  $Q_{st}$  of CO<sub>2</sub> in NUS-6(Hf) (27.7 kJ mol<sup>-1</sup>) is indeed higher than that in NUS-6(Zr) (24.8 kJ mol<sup>-1</sup>). The  $CO_2/N_2$  selectivity of NUS-6 was further evaluated using ideal adsorption solution theory (IAST), in which the single gas isotherms were used to predict the selectivity of the mixed gas.<sup>51</sup> Similar to the trend of Q<sub>st</sub>, NUS-6(Hf) also has an IAST  $CO_2/N_2$  selectivity higher than that of NUS-6(Zr) [30.2 vs 21.7 (Figure 6c)], confirming the importance of CO<sub>2</sub>-MOFs interactions. The high density of the polar sulfonic acid group in NUS-6 suggests a hydroscopic property, which is proven by the quasi-type I water vapor sorption isotherms where large amounts of water uptake are observed at a  $P/P_0$  of <0.3 (Figure 6d). Such a hydroscopic property of NUS-6 may suggest high water interference for CO<sub>2</sub> capture. Therefore, dehydration of flue gas should be processed beforehand were these materials to be used as adsorbents for postcombustion CO<sub>2</sub> capture.<sup>39</sup>

The hierarchical porosity, high stability, and hybrid Brønsted/Lewis acidity suggest that NUS-6 should be efficient heterogeneous catalysts. Their catalytic performance was evaluated on the basis of the dehydration of fructose into 5-hydroxymethylfurfural (HMF), which is an important process in biomass conversion and is typically catalyzed by Brønsted acids such as sulfonic acids or solid acids.<sup>52–54</sup> We initially attempted this reaction using water as the solvent, but with a negligible yield of HMF (~5%). Therefore, further attempts were performed using dimethyl sulfoxide (DMSO) as the solvent whose positive role for this reaction has been proven previously.<sup>55–57</sup> We started with NUS-6(Zr) using a loading amount of 3.5 mol % similar to the value from the literature.<sup>27</sup>

#### Table 1. Catalytic Dehydration of Fructose to HMF

HOH		)H :H₂OH <sup>-</sup>	Catal	yst → онс		он
	HÖ Fructose		DMSO		HMF	
					HMF	
entry	catalyst loading (mol %)	temp (°C)	time (h)	fructose conversion (%)	selectivity (%)	yield (%)
1 <sup><i>a</i></sup>	3.5	80	1	<5	nd	<5
2 <sup><i>a</i></sup>	3.5	100	1	>99	84	84
3 <sup><i>a</i></sup>	3.5	120	1	>99	72	72
4 <sup><i>a</i></sup>	5	100	1	>99	69	69
5 <sup>a</sup>	1.75	100	1	77	51	39
6 <sup><i>a</i></sup>	3.5	100	0.5	75	72	54
$7^a$	3.5	100	1.5	>99	71	71
8 <sup>b</sup>	_	100	1	5	nd	nd
9 <sup>c</sup>	3.5	100	1	>99	62	62
10 <sup>d</sup>	3.5	100	1	>99	98	98
11 <sup>e</sup>	3.5	100	1	5	nd	nd
12 <sup>f</sup>	3.5	100	1	12	67	8
<sup>4</sup> NUS-6 66(Hf).	6(Zr). <sup>b</sup> No cat	talyst. <sup>c</sup> D	MST. <sup>d</sup>	NUS-6(Hf). <sup>e</sup>	UiO-66(Zr).	<sup>f</sup> UiO-

1-3). NUS-6(Zr) exhibits an almost quantitative conversion of fructose (>99%) with a high chemoselectivity (84%) and yield (84%) of HMF at 100 °C. The HMF yield is comparable to that of postsynthetically sulfonated microporous UiO-66(Zr) (85%), while the latter reaction was performed at a higher temperature of 120 °C.<sup>27</sup> By increasing the reaction temperature from 100 to 120  $^\circ$ C, we observed that the HMF selectivity decreased from 84 to 72%. This is different from the continuous increase in HMF yield with the increase in temperature from 100 to 140 °C reported by Chen et al.<sup>27</sup> Meanwhile, NUS-6(Hf) also exhibits a similar trend of reduced HMF yield at higher temperatures from 98% to 89%. This can be attributed to the stronger acidity of NUS-6 MOFs (higher concentration of -SO<sub>3</sub>H groups) that further convert HMF to other byproducts (e.g., alcohols) at high temperatures as HMF is inherently not stable, especially at high temperatures.<sup>55,58</sup> Increasing the loading of NUS-6(Zr) to 5 mol % results in a reduced HMF yield (69%), possibly because of the intensified side reactions (Table 1, entry 4), while decreasing NUS-6(Zr) loading to 1.75 mol % leads to a lower fructose conversion (77%) and HMF yield (39%) caused by insufficient catalysis (Table 1, entry 5). The reaction time was further optimized

with fixed reaction temperature (100 °C) and NUS-6(Zr) loading (3.5 mol %), proving that a reaction duration of 1 h gives the best results under such conditions (Table 1, entries 6 and 7). A control experiment without any catalyst afforded <5% fructose conversion with a negligible HMF yield (Table 1, entry 8), confirming the critical role of NUS-6(Zr) as the catalyst. In comparison, dimethyl 2-sulfoterephthalate (DMST) was used as a homogeneous catalyst for this reaction under a similar reaction condition (3.5 mol % loading, 100 °C, 1 h), resulting in a quantitative fructose conversion but worse chemoselectivity (62%) and yield (62%) of HMF (Table 1, entry 9), suggesting rampant side reactions that can be mitigated using NUS-6(Zr) as the heterogeneous catalyst.

When NUS-6(Hf) was used as the catalyst under a similar reaction condition, a quantitative conversion of fructose (>99%) was obtained along with extremely high chemoselectivity (98%) and yield (98%) of HMF (Table 1, entry 10). This result is better than those of NUS-6(Zr) (84% chemoselectivity and 84% yield) and other postsynthetically sulfonated MOFs such as MIL-53(Al) (80% chemoselectivity and ~79% yield), UiO-66(Zr) (~86% chemoselectivity and ~85% yield), and MIL-101(Cr) (91% chemoselectivity and ~90% yield).27 To the best of our knowledge, NUS-6(Hf) represents the most efficient and selective solid acid catalyst for this reaction so far.<sup>54</sup> We also examined the heterogeneity and recyclability of NUS-6(Hf). The supernatant of the reaction media obtained by using a regular filter during the dehydration reaction did not yield any additional product, indicating the role of the heterogeneous catalyst played by NUS-6(Hf) (Figure 7).



Figure 7. Kinetic study of dehydration of fructose into HMF via the catalysis of various catalysts.

Upon completion of the reaction, NUS-6(Hf) could be recovered in quantitative yield and used repeatedly without a significant loss of catalytic activity for the three subsequent runs (quantitative fructose conversion with 94, 92, and 90% yields of HMF for one, two, and three additional runs, respectively). Recycled NUS-6(Hf) retains its high crystallinity (Figure S9) but with compromised porosity possibly due to the trapping of reagents in the framework that are hard to remove during regeneration (Figure S10).

To further study the superior catalytic activity of NUS-6(Hf) over NUS-6(Zr) and their homogeneous counterpart DMST, we performed the kinetic study of this reaction using 3.5 mol % loading of catalysts at 100  $^{\circ}$ C for a continuous period of 1 h

(Figure 7). When DMST was used as the catalyst, the reaction had a fast kinetics with quantitative fructose conversion obtained after ~10 min, while the desired HMF yield was moderate (75%) and started to decline to 62% in the end because of uncontrollable side reactions caused by homogeneous catalysts.<sup>57</sup> On the other hand, both NUS-6(Hf) and NUS-6(Zr) displayed remarkably enhanced catalytic activity and chemoselectivity, with slower but steady increases in both fructose conversion and HMF yield within 1 h. The slower reaction kinetics of NUS-6 MOFs can be explained by the restricted mass transfer within porous media, which on the other hand might restrain the unwanted side reactions leading to higher HMF yields. Compared to those of NUS-6(Zr), NUS-6(Hf) demonstrated both faster reaction kinetics and a higher HMF yield. Given the similar crystal structure between these two MOFs, the difference in catalytic performance can be attributed to the extra Brønsted acidity in NUS-6(Hf) caused by polarized  $\mu_3$ -OH groups in Hf clusters.<sup>20</sup> In a control experiment, pristine UiO-66(Zr) and UiO-66(Hf) without any sulfonic acid groups were used as the catalyst for the reaction described above. As a result, UiO-66(Zr) was almost completely feckless (Table 1, entry 11) while UiO-66(Hf) exhibited a measurable catalytic activity (Table 1, entry 12), partially confirming the Brønsted acidity in Hf-containing MOFs. Acid-base titration experiments were conducted to quantify the Brønsted acid concentration. Before titration, an aqueous NaCl solution was used as an ion-exchange reagent to release the acidic protons from MOFs into the solution, which was later titrated after the removal of MOFs.<sup>30</sup> Compared to direct titration of MOF suspensions, this method can avoid MOF decomposition during titration with more accurate reading. However, it is based on the kinetic equilibrium of cation exchange and can detect only those Na<sup>+</sup> accessible acidic protons with low  $pK_a$  values (large dissociation constants). UiO-66(Zr) was titrated as a blank compare, which surprisingly exhibited a mild Brønsted acidity of 0.01 mol mol<sup>-1</sup> (mole of acidic proton per mole of MOFs based on molecular formula) (Figure 8). Because formic acid was used as the modulator during the synthesis of UiO-66(Zr), the mild Brønsted acidity may come from the residual formic acid trapped inside the framework. Compared to UiO-66(Zr), UiO-66(Hf) has 5 times more acidic protons ( $0.06 \text{ mol mol}^{-1}$ ), which strongly suggests its higher Brønsted acidity is contributed by the  $\mu_3$ -OH groups, which also explains its catalytic activity in fructose dehydration.



Figure 8. Concentrations of acidic protons in various MOFs obtained by acid-base titration.

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Because of the sulfonic acid groups, the acidic proton concentration of NUS-6(Zr) is much higher (12.9 mol mol<sup>-1</sup>), while NUS-6(Hf) exhibited an even higher acidic proton concentration (13.9 mol mol<sup>-1</sup>), which might due to the extra Brønsted acidity contributed by  $\mu_3$ -OH groups as well as the easier dissociation of acidic protons caused by oxophilic Hf cations. However, the measured acidic proton concentrations of NUS-6 MOFs are still lower than the theoretical value of 15 mol mol<sup>-1</sup> contributed solely by the sulfonic acid groups, suggesting that not all the acidic protons can be replaced by Na<sup>+</sup> possibly because of (1) insufficient equilibrium time, (2) different dissociation constants of available acidic protons, (3) steric hindrance caused by partial framework collapse, and (4) trapping of protons by defect-containing Zr or Hf clusters.<sup>36</sup>

Besides the stronger Brønsted acidity, a more suitable pore size might be another factor in determining the superior catalytic activity of NUS-6(Hf) versus that of NUS-6(Zr) for dehydration of fructose into HMF. It is widely accepted that this reaction starts from the fructofuranosyl form of fructose.<sup>5</sup> Many Brønsted acids are able to promote this trans-formation,<sup>57,60-62</sup> but selectivity for HMF could seldom reach 98% as in NUS-6(Hf) mainly because of the severe side reaction of humin formation via aldol condensation.<sup>63</sup> We have noticed that the smallest pore of NUS-6(Hf) has a diameter of ~5.5 Å (Figure 4b), which is only slightly larger than the hydrodynamic radius of monosaccharides (~4 Å).<sup>64</sup> Therefore, the guest fructose molecules can be well-confined within the smallest pores of NUS-6(Hf), which might prevent isomerization of fructose from its naturally predominant furanosyl form to the linear form, leading to an increase in the reaction rate. More importantly, the fructofuranosyl form disfavors byproduct formation as it does not contain a carbonyl group, which is responsible for the undesired aldol condensation. To the best of our knowledge, the utilization of the pore confinement effect in MOFs to simultaneously enhance reaction rate as well as inhibit side reactions for biomass conversion as demonstrated in this study is unprecedented.

## CONCLUSION

In summary, we have directly synthesized two sulfonated MOFs named NUS-6(Zr) and NUS-6(Hf) via the modulated hydrothermal (MHT) approach at a low reaction temperature of 80 °C. Rietveld refinements of synchrotron PXRD data reveal hierarchically porous structures stemming from a parental UiO-66 topology with missing ligands and clusters. Unlike the previously reported sulfonated Zr MOFs, NUS-6(Zr) and NUS-6(Hf) exhibit excellent stability and can retain their porosity under vigorous activation at 150 °C, possibly because of the stable crystalline subparticles caused by reversed crystal growth. These MOFs exhibited decent CO<sub>2</sub> capture performance and were used as solid acid catalysts for dehydration of fructose to 5-hydroxymethylfurfural (HMF), in which NUS-6(Hf) exhibited better reaction kinetics and chemoselectivity with quantitative fructose conversion and a HMF yield of 98% that make it one of the best heterogeneous catalysts for such conversion. The superior catalytic activity of NUS-6(Hf) was attributed to its stronger Brønsted acidity as well as more suitable pore size that can inhibit side reactions. Acid-base titration experiments were used to experimentally prove the superior Brønsted acidity of Hf-MOFs. Our results have demonstrated for the first time the uniqueness of HfMOFs featuring superior stability and Brønsted acidity that can be applied as solid acid catalysts in biobased chemical synthesis.

## ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.6b00139.

Experimental procedures, calculations, EDS elemental mapping, gas sorption isotherms, etc. (PDF)

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#### Notes

The authors declare the following competing financial interest(s): A U.S. provisional patent (62/132,608) has been filed on March 13, 2015, based on the presented result.

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