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Superacidity in Sulfated Metal-Organic Framework-808 8 h 32

ABSTRACT: Superacids, defined as acids with a Hammett acidity function  $H_0 < -12$ , are useful materials, but a need exists for new, designable solid

Siêu axit trong vật liệu khung kim loại-hữu cơ sulfate hóa

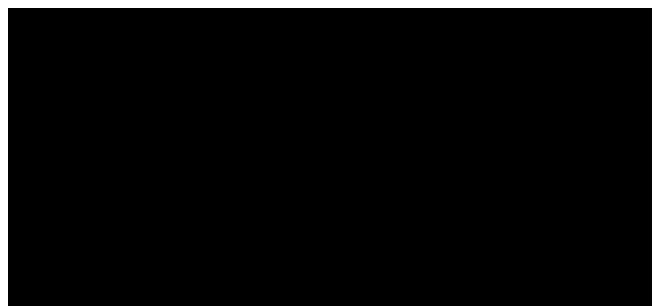
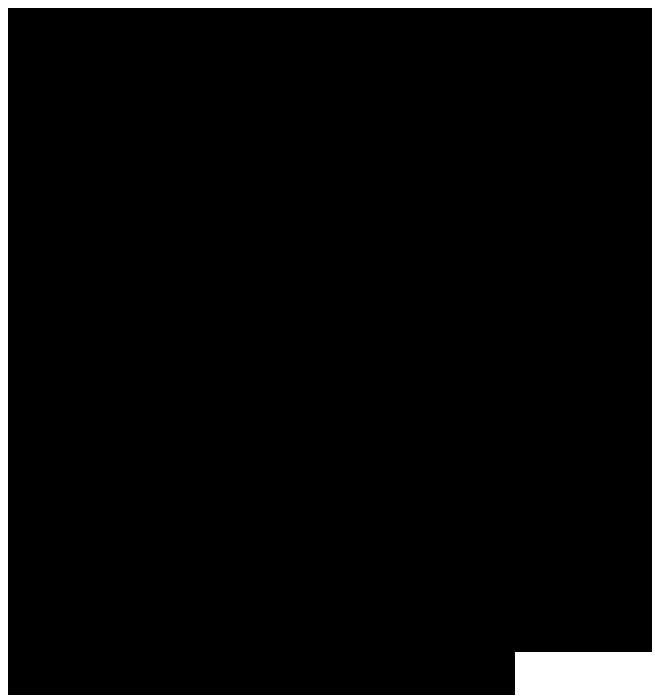
TÓM TẮT: Theo định nghĩa, các siêu axit là những axit có hàm axit Hammett  $H_0 < -12$ , đây là những vật liệu có ích, nhưng hiện nay chúng ta đang cần các hệ trạng

state systems. Here, we report superacidity in a sulfated metal-organic framework (MOF) obtained by treating the microcrystal-line form of MOF-808 [MOF-808-P:  $Zr_6O_5(OH)_3(BTC)_2(HCOO)_5(H_2O)_2$ , BTC = 1,3,5-benzenetricarbox-ylate] with aqueous sulfuric acid to generate its sulfated analogue, MOF-808-2.5S04 [ $Zr_6O_5(OH)_3(BTC)_2(SO_4)_{25}(H_2O)_{25}$ ]. This material has a Hammett acidity function  $H_0 < -14.5$  and is thus identified as a superacid, providing the first evidence for superacidity in MOFs. The superacidity is attributed to the presence of zirconium-bound sulfate groups structurally characterized using single-crystal X-ray diffraction analysis.

Superacids are acids stronger than 100% sulfuric acid,<sup>1</sup> that is, acids having Hammett acidity functions  $H_0 < -12.2$ . Liquid superacids such as HF-SbF<sub>5</sub>,<sup>3</sup> HSO<sub>3</sub>F<sub>1b</sub> and CF<sub>3</sub>SO<sub>3</sub>H<sup>4</sup> are extremely reactive and are capable of activating hydrocarbons at ambient temperature.<sup>5</sup> Solid superacids such as sulfated zirconia,<sup>6</sup> Nafion-H,<sup>7</sup> and the zeolite HY<sup>8</sup> offer advantages over their liquid analogues due to their ease of handling and diminished environmental threat.<sup>9</sup> However, challenges still remain in this chemistry concerning the precise determination of the level of acidity, knowledge of the nature of the acid sites, and the discovery of new designable superacid systems.

Metal-organic frameworks (MOFs) have a great potential for the development of new solid superacids due to their structural diversity, crystalline structure, and tunable porosity.<sup>10</sup> Robust, acid-stable MOFs displaying Bronsted acidity have been

thái rắn mới, kiểm soát được. Ở đây, chúng tôi trình bày hoạt tính siêu axit trong vật liệu khung kim loại-hữu cơ (MOF) được chế tạo bằng cách xử lý dạng vi tinh thể của MOF-808 [MOF-808-P:  $Zr_6O_5(OH)_3(BTC)_2(HCOO)_5(H_2O)_2$ , BTC = 1,3,5-benzenetricarbox-ylate] bằng dung dịch axit sulfuric để tạo dạng sunfat hóa của nó, MOF-808-2.5S04 [ $Zr_6O_5(OH)_3(BTC)_2(SO_4)_{25}(H_2O)_{25}$ ]. Vật liệu này có hàm axit Hammett axit  $H_0 < -14,5$  và do đó được xếp vào loại vật liệu siêu axit, minh chứng thực nghiệm đầu tiên về hoạt tính siêu axit trong các MOF. Tính siêu axit của vật liệu này được quy cho các nhóm sulfate liên kết với zirconium- được xác định qua phép phân tích nhiễu xạ tia X đơn tinh thể.



prepared by utilizing sulfonated organic linkers or hydroxyl and water ligands coordinated to metal sites within the framework.<sup>11</sup> The acidity of these MOFs is either undetermined<sup>11a,d,f</sup> or has been measured from the shift of the -OH group vibration induced by CO adsorption and found to have  $H_0 = -3$  to  $-8$ ; <sup>11b</sup> none have displayed superacidity (i.e.,  $H_0 < -12$ ). Here, we show that superacidity can be achieved by treating a microcrystalline powder of the Zr(IV) MOF-808<sup>12</sup> [mOF-808-P:Zr<sub>6</sub>O<sub>5</sub>(OH)<sub>3</sub>(BTC)<sub>2</sub>(HCOO)<sub>5</sub>(H<sub>2</sub>O)<sub>2</sub>, BTC = 1,3,5-

benzenetricarboxylate] with aqueous sulfuric acid. The resulting sulfated MOF-808 [MOF-808-2.5SO<sub>4</sub>:Zr<sub>6</sub>O<sub>5</sub>(OH)<sub>3</sub>(BTC)<sub>2</sub>(SO<sub>4</sub>)<sub>2.5</sub>(H<sub>2</sub>O)<sub>2.5</sub>] has  $H_0 < -14.5$  by the Hammett indicator method, a value corresponding to a higher acidity than 100% sulfuric acid ( $H_0 = -12$ ), providing, for the first time, evidence of superacidity in MOFs. The presence of sulfate units bound to the Zr centers of the MOF was established by single crystal X-ray diffraction and IR spectroscopy. We believe these studies serve as a benchmark for producing and measuring superacidity in MOFs.

In the crystal structure of MOF-808,<sup>12</sup> each Zr secondary building unit (SBU), Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(-CO<sub>2</sub>)<sub>6</sub>(HCOO)<sub>6</sub>, is linked to six BTC units to form a 3-D porous framework containing two different types of pores (Figure 1). The smaller, tetrahedral pore is inaccessible to guests because of its small, 1.2-Å aperture diameter, while the larger, adamantane-shaped pore has a much larger internal pore and aperture diameters of 18 and 14 Å, respectively. Since all the formate ligands are

accessible through the large pore, we believed they could be replaced by sulfate ligands. Furthermore, the formate ligands would be far more reactive than the BTC linkers since they are connected to only one as opposed to three Zr SBUs.

Our studies were carried out on a new microcrystalline form of MOF-808 designated MOF-808-P, which was prepared on a 5-g scale using a modified version of the single-crystal MOF-808 synthesis (Supporting Information, SI, Section S1).<sup>12</sup> MOF-808-P formed more rapidly than MOF-808 and was obtained as powders of 200-800-nm-sized, octahedral microcrystals (Figure 2a). Phase purity and porosity were established using powder X-ray diffraction (PXRD) and nitrogen sorption measurements (Figure 2b,c), respectively, and its chemical composition was found to include five instead of six formate ligands per Zr SBU using elemental analysis and integrated <sup>1</sup>H NMR spectra of samples digested in a mixture of HF and DMSO-d<sub>6</sub> (SI, Section S1). It is likely that the missing formate group was replaced by the solvent used in the synthesis (DMF) or water.

Sulfation of MOF-808-P was achieved by submersion in different concentrations of aqueous sulfuric acid for 1 day (SI, Section S1). In each case, 500 mg of MOF-808-P were added to 50 mL of 0.005-0.1 M aqueous sulfuric acid and the resulting

Figure 1.  $Zr_6O_4(OH)_4(-CO_2)_6(HCOO)_6$  secondary building units (SBUs) are combined with BTC linkers to form MOF-808, which has a

porous, three-dimensional framework containing large adamantane-shaped cages (open) and small tetrahedral cages (filled with green spheres). Atom labeling scheme: formate C and O atoms, black and red spheres, respectively; other C and O atoms, gray and pink spheres, respectively; Zr coordination polyhedra, blue. H atoms are omitted for clarity.

suspension was stirred for 1 min about once every 2 h. The crystal shape and color of these crude products were the same as those of MOF-808-P according to scanning electron microscopy (SEM) (Figures 2a, S3) and optical microscopy, respectively. These crude reaction products were treated with acetone and chloroform and then dried at ambient and elevated temperature under vacuum to obtain final products, which were stored in an inert atmosphere to avoid hydration. The final products displayed PXRD patterns coincident with those of the original unsulfated MOF-808-P material and, remarkably, nearly identical porosities (Figures 2b,c, S2, and S4-S8). They were formulated using elemental analysis and integrated solution  $^1\text{H}$  NMR spectra of digested samples (SI, Section S1). Replacement of formate by sulfate was monitored in this fashion (Table 1), and the different materials were designated MOF-808- $x\text{SO}_4$ ,  $x = 0.65, 1.3, 2.3, \text{ and } 2.5$ , where  $x = \text{number of sulfate groups per SBU}$ . Note that the crystallinity of the sulfated framework, its porosity, and its superacidity (see below) could not be obtained if the aqueous solvent was removed directly from the pores of the initial reaction product by application of heat and vacuum. Instead, they required

removal of the water molecules in the MOF pores by solvent exchange with acetone and chloroform followed by evacuation, first at room temperature and then at elevated temperature.

Initial evidence for metal-bound sulfate groups was obtained from IR spectra of sulfated MOFs, where bands were observed between 800 and 1500  $\text{cm}^{-1}$  that were not observed in spectra of unsulfated MOF-808-P and could be assigned to sulfate ligands (Figure S9).<sup>13</sup> An X-ray diffraction study of an MOF-808-2.3SO<sub>4</sub> single crystal provided unequivocal evidence for metal-bound sulfate groups incorporated into a crystalline, porous MOF (Figure 2d, SI, Section S2). In the MOF-808 framework, ~2.4 bound sulfates were observed per Zr SBU.<sup>14</sup>

The acidity of MOF-808-xSO<sub>4</sub> was examined using standard catalytic acid/base test reactions. First, cyclization of citronellal to isopulegol was studied (Scheme S1).<sup>11c'15</sup> The product distribution of this reaction is known to be sensitive to the nature of the acid sites:

with Lewis acids only, high selectivity (>75%) toward ( $\pm$ )-isopulegol is obtained,

while, with Brønsted acids, the selectivity is significantly lower.<sup>15</sup> The MOF-808 materials, despite their nearly identical structural frameworks and porosities, displayed selectivity toward ( $\pm$ )-isopulegol that decreased monotonically with increasing x from 85% in MOF-808-P to 55% in MOF-808-2.5SO<sub>4</sub> (Table 1). This result indicates that Brønsted acidity was introduced into MOF-808-xSO<sub>4</sub> during sulfuric acid treatment, leading to

decreased product selectivity. A similar result was obtained from a study of acid-catalyzed  $\alpha$ -pinene isomerization, which typically requires strong acid catalysts (Scheme S2).<sup>16</sup> No conversion of  $\alpha$ -pinene was observed for MOF-808-P or MOF-808-0.65SO<sub>4</sub>. Yet,  $\alpha$ -pinene conversion was quantitative using MOF-808-2.5SO<sub>4</sub> (Table 1), where selectivity toward camphene and limonene was similar to that observed for sulfated zirconia.<sup>16a,b</sup> These findings indicate the presence of strongly acidic sites in MOF-808-2.5SO<sub>4</sub>.

The qualitative catalytic tests of MOF-808-xSO<sub>4</sub> acidity just mentioned were supplemented with more quantitative probes. First, the Hammett indicator base method was employed. This method<sup>17</sup> has been used to assess the acidity of solids such as zeolites<sup>18</sup> and sulfated zirconia.<sup>19</sup> Here, if immersion of a solid in a specific indicator solution changes the color of the solid to that of the acid form of the indicator, the H<sub>0</sub> value of that solid is the same or lower than the pK<sub>a</sub> of the conjugate acid of the indicator. While MOF-808-P and MOF-808-0.65SO<sub>4</sub> displayed relatively low acidity (H<sub>0</sub> > 2.8) and moderate acidity (-4.4 > H<sub>0</sub> > -5.9), respectively, MOF-808-1.3SO<sub>4</sub> and MOF-808-2.5SO<sub>4</sub> displayed a color change even in a benzene solution of 2,4-dinitrofluorobenzene, indicating H<sub>0</sub> < -14.5 and placing these MOFs in the superacid region (H<sub>0</sub> < -12) (Table 1). This result is consistent with the results of catalytic  $\alpha$ -pinene isomerization, where only MOF-808-1.3SO<sub>4</sub> and MOF-808-2.5SO<sub>4</sub> displayed appreciable yields of camphene and limonene. Both MOF-808-1.3SO<sub>4</sub> and MOF-808-2.5SO<sub>4</sub>

showed lower acidity ( $\text{H}0 > 2.8$ ) following exposure to atmospheric moisture.

The development of acidity in sulfated MOF-808 was confirmed in a  $^{31}\text{P}$  MAS NMR spectroscopic study of adsorbed trimethylphosphine oxide probe molecules.<sup>20</sup> Trimethylphosphine oxide (TMPO) was chosen as a trialkylphosphine oxide probe because of its suitable size for diffusion in MOF pores. The  $^{31}\text{P}$  NMR chemical shift of TMPO molecules adsorbed on Bronsted acid sites is known to shift downfield with increasing acid strength.<sup>20c</sup> Spectra of TMPO adsorbed on MOF-808-P and MOF-808-xS<sub>04</sub> samples are shown in Figure S10. For MOF-808-P, two resonances assigned to adsorbed TMPO appeared at 62 and 56 ppm and a third resonance assigned to free TMPO trapped in the MOF pores appeared at 43 ppm.<sup>20c</sup> The same three resonances were observed in spectra of MOF-808-0.65S<sub>04</sub>, albeit with different relative intensities. However, a new resonance appeared at 69 ppm in spectra of MOF-808-1.3S<sub>04</sub> and MOF-808-2.5S<sub>04</sub>. Since the appearance of this new peak correlates with the observation of  $\alpha$ -pinene conversion, the 69 ppm resonance was assigned to TMPO adsorbed on a strongly acidic site. In support of this assignment, exposure of MOF-808-2.5S<sub>04</sub> to atmospheric moisture caused the 69 ppm resonance to lose almost all of its intensity in the same way that MOF-808-2.5S<sub>04</sub> loses its ability both to isomerize  $\alpha$ -pinene and to display Hammett superacidity after exposure to atmospheric moisture.



In a preliminary survey of reactions, MOF-808-2.5S04 was found to be catalytically active in various acid-catalyzed reactions including Friedel-Crafts acylation, esterification, and isomerization (Table 2), as well as in the conversion of methyl-

Table 2. Various Reactions Catalyzed by MOF-808-2.5S04

"250 mg of MOF-808-2.5S04, 5 mL of anisole, 50 mg of benzoic acid, 110 °C, 12 h. b50 mg of MOF-808-2.5S04, 5 mL of anisole, 100 mg of benzoic anhydride, 110 °C, 12 h. c50 mg of MOF-808-2.5S04, 5 mL of anisole, 350 mg of 2-chlorobenzoyl chloride, 110 °C, 12 h. d200 mg of MOF-808-2.5S04, 10 mL of methanol, 1 g of oleic acid, 65 °C, 6 h. e150 mg of MOF-808-2.5S04, 2.5 mL of limonene, 60 °C, 1 h.

cyclopentane (MCP) into various hydrocarbons at 150-200 °C, the latter being a test reaction for catalytic reforming (Scheme S6).<sup>21</sup> Efforts are underway to optimize such reactions and fully exploit the potential of these new materials.

#### ■ ASSOCIATED CONTENT Supporting Information

Details of synthesis and characterization, crystal structure analysis tables, PXRD patterns, SEM images, gas adsorption isotherms, IR spectra, Hammett indicator tests, <sup>31</sup>P MAS solid-state NMR spectra, and catalytic tests. This material is available free of charge via the Internet at <http://pubs.acs.org>.