

Superacidity in Sulfated Metal–Organic Framework-808

Juncong Jiang,^{†,‡} Felipe Gándara,^{†,‡} Yue-Biao Zhang,^{†,‡} Kyungsu Na,^{†,§} Omar M. Yaghi,^{*,†,‡,||} and Walter G. Klemperer^{*,†,Δ}

[†]Department of Chemistry, University of California, Berkeley and Kavli Energy NanoSciences Institute at Berkeley, Berkeley, California 94720, United States

[‡]Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

[§]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

^{||}King Fahd University of Petroleum and Minerals, Dhahran 34464, Saudi Arabia

^ΔDepartment of Chemistry, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801, United States

S Supporting Information

ABSTRACT: Superacids, defined as acids with a Hammett acidity function $H_0 \leq -12$, are useful materials, but a need exists for new, designable solid state systems. Here, we report superacidity in a sulfated metal–organic framework (MOF) obtained by treating the microcrystalline form of MOF-808 [MOF-808-P: $Zr_6O_5(OH)_3(BTC)_2(HCOO)_5(H_2O)_2$, BTC = 1,3,5-benzenetricarboxylate] with aqueous sulfuric acid to generate its sulfated analogue, MOF-808-2.5SO₄ [$Zr_6O_5(OH)_3(BTC)_2(SO_4)_{2.5}(H_2O)_{2.5}$]. This material has a Hammett acidity function $H_0 \leq -14.5$ 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,¹ that is, acids having Hammett acidity functions $H_0 \leq -12$.² Liquid superacids such as HF-SbF₅,³ HSO₃F^{1b} and CF₃SO₃H⁴ are extremely reactive and are capable of activating hydrocarbons at ambient temperature.⁵ Solid superacids such as sulfated zirconia,⁶ Nafion-H,⁷ and the zeolite HY⁸ offer advantages over their liquid analogues due to their ease of handling and diminished environmental threat.⁹ 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.¹⁰ Robust, acid-stable MOFs displaying Brønsted acidity have been prepared by utilizing sulfonated organic linkers or hydroxyl and water ligands coordinated to metal sites within the framework.¹¹ The acidity of these MOFs is either undetermined^{11a,d,f} 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 ;^{11b} none have displayed superacidity (i.e., $H_0 \leq -12$). Here, we show that superacidity can be achieved by treating a microcrystalline powder of the Zr(IV) MOF-808¹² [MOF-808-P: $Zr_6O_5(OH)_3(BTC)_2(HCOO)_5(H_2O)_2$, BTC = 1,3,5-

benzenetricarboxylate] with aqueous sulfuric acid. The resulting sulfated MOF-808 [MOF-808-2.5SO₄: $Zr_6O_5(OH)_3(BTC)_2(SO_4)_{2.5}(H_2O)_{2.5}$] has $H_0 \leq -14.5$ 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-808,¹² each Zr secondary building unit (SBU), $Zr_6O_4(OH)_4(-CO_2)_6(HCOO)_6$, 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).¹² 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 ¹H NMR spectra of samples digested in a mixture of HF and DMSO-*d*₆ (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

Received: July 14, 2014

Published: August 26, 2014

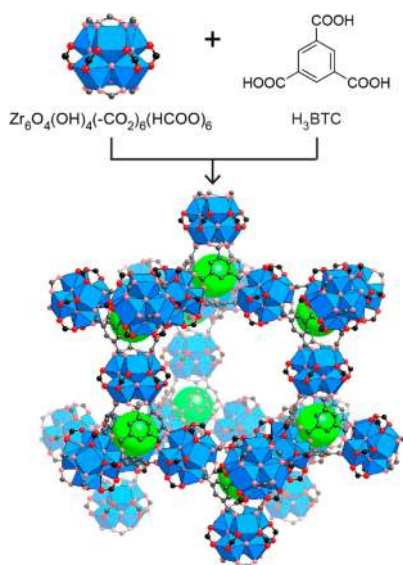


Figure 1. $\text{Zr}_6\text{O}_4(\text{OH})_4(-\text{CO}_2)_6(\text{HCOO})_6$ secondary building units (SBUs) are combined with BTC linkers to form MOF-808, which has a porous, three-dimensional framework containing large adamantane-shaped cages (open) and small tetrahedral cages (filled with green spheres). 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 ^1H 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- $x\text{SO}_4$, $x = 0.65, 1.3, 2.3,$ and 2.5 , where $x =$ 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 cm^{-1} that were not observed in spectra of unsulfated MOF-808-P and could be assigned to sulfate ligands (Figure S9).¹³ An X-ray diffraction study of an MOF-808- 2.3SO_4 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.¹⁴

The acidity of MOF-808- $x\text{SO}_4$ was examined using standard catalytic acid/base test reactions. First, cyclization of citronellal to isopulegol was studied (Scheme S1).^{11c,15} The product distribution of this reaction is known to be sensitive to the nature of the acid sites: with Lewis acids only, high selectivity ($\geq 75\%$) toward (\pm)-isopulegol is obtained, while, with Brønsted acids, the selectivity is significantly lower.¹⁵ 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_4 (Table 1). This result indicates that Brønsted acidity was introduced into MOF-808- $x\text{SO}_4$ during sulfuric acid treatment, leading to decreased

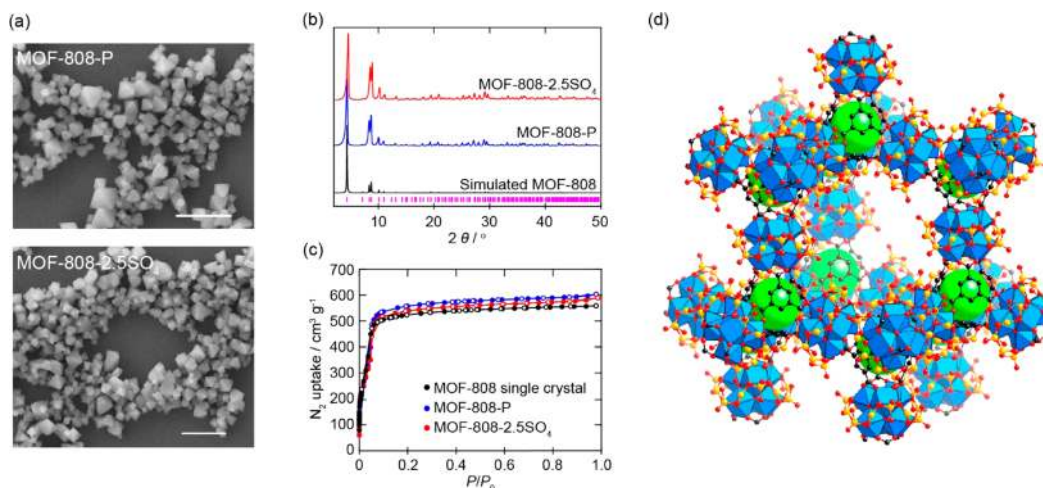


Figure 2. (a) SEM images for MOF-808-P and MOF-808- 2.5SO_4 (scale bar: $2\ \mu\text{m}$). (b) Comparison of experimental powder X-ray diffraction patterns of MOF-808-P (blue) and MOF-808- 2.5SO_4 (red) with simulated pattern (black) calculated from the single-crystal structure of MOF-808.¹² (c) Nitrogen adsorption isotherms for MOF-808 single crystal (black), MOF-808-P (blue), and MOF-808- 2.5SO_4 powder (red) at 77 K with adsorption and desorption branches represented by closed and open circles, respectively. P/P_0 , relative pressure. (d) Fragment of the MOF-808- 2.3SO_4 crystal structure obtained from a single-crystal X-ray diffraction study. The disordered sulfate groups have a chemical occupancy of 0.2. Two O atoms in one of the sulfate groups could not be located from the residual electron density maps. C, O, and S atoms are represented by black, red, and yellow spheres, respectively; Zr coordination polyhedra are blue. Green spheres enclose the space within the tetrahedral cages. H atoms are omitted for clarity.

Table 1. Summary of MOF-808- x SO₄ Composition, Catalytic Performance, and Acidity

Material	Composition ^a		Citronellal cyclization ^c		α -Pinene isomerization ^e			Hammett acidity H_0 ^g
	Formate ^b	Sulfate ^b	Citronellal conversion, %	(\pm)-Isopulegol selectivity, %	α -Pinene conversion, %	Camphene selectivity, %	Limonene selectivity, %	
MOF-808-P	5.0	0	8.0	85	0	–	–	≥ 2.8
MOF-808-0.65SO ₄	3.0	0.65	44	78	0	–	–	–4.4 to –5.9
MOF-808-1.3SO ₄	1.8	1.3	97 ^d	67	31	55	18	≤ -14.5
MOF-808-2.5SO ₄	<0.1	2.5	98 ^d	55	99 ^f	56	16	≤ -14.5

^aFrom elemental analysis and solution ¹H NMR spectra of digested MOFs (SI, Section S1). ^bNumber per zirconium SBU. ^c50 mg of MOF-808- x SO₄, 1.5 mL of (\pm)-citronellal, 5 mL of toluene, 60 °C, 8 h. ^dReaction time: 1.5 h. ^e100 mg of MOF-808- x SO₄, 3 mL of α -pinene, 120 °C, 2 days. ^fReaction time: 1.5 days. ^gMeasured using Hammett indicators (SI, Section S7).

product selectivity. A similar result was obtained from a study of acid-catalyzed α -pinene isomerization, which typically requires strong acid catalysts (Scheme S2).¹⁶ No conversion of α -pinene was observed for MOF-808-P or MOF-808-0.65SO₄. Yet, α -pinene conversion was quantitative using MOF-808-2.5SO₄ (Table 1), where selectivity toward camphene and limonene was similar to that observed for sulfated zirconia.^{16a,b} These findings indicate the presence of strongly acidic sites in MOF-808-2.5SO₄.


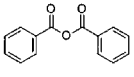

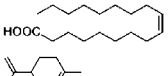

The qualitative catalytic tests of MOF-808- x SO₄ acidity just mentioned were supplemented with more quantitative probes. First, the Hammett indicator base method was employed. This method¹⁷ has been used to assess the acidity of solids such as zeolites¹⁸ and sulfated zirconia.¹⁹ Here, if immersion of a solid in a specific indicator solution changes the color of the solid to that of the acid form of the indicator, the H_0 value of that solid is the same or lower than the pK_a of the conjugate acid of the indicator. While MOF-808-P and MOF-808-0.65SO₄ displayed relatively low acidity ($H_0 \geq 2.8$) and moderate acidity ($-4.4 \geq H_0 \geq -5.9$), respectively, MOF-808-1.3SO₄ and MOF-808-2.5SO₄ displayed a color change even in a benzene solution of 2,4-dinitrofluorobenzene, indicating $H_0 \leq -14.5$ and placing these MOFs in the superacidic region ($H_0 \leq -12$) (Table 1). This result is consistent with the results of catalytic α -pinene isomerization, where only MOF-808-1.3SO₄ and MOF-808-2.5SO₄ displayed appreciable yields of camphene and limonene. Both MOF-808-1.3SO₄ and MOF-808-2.5SO₄ showed lower acidity ($H_0 \geq 2.8$) following exposure to atmospheric moisture.

The development of acidity in sulfated MOF-808 was confirmed in a ³¹P MAS NMR spectroscopic study of adsorbed trimethylphosphine oxide probe molecules.²⁰ Trimethylphosphine oxide (TMPO) was chosen as a trialkylphosphine oxide probe because of its suitable size for diffusion in MOF pores. The ³¹P NMR chemical shift of TMPO molecules adsorbed on Brønsted acid sites is known to shift downfield with increasing acid strength.^{20c} Spectra of TMPO adsorbed on MOF-808-P and MOF-808- x SO₄ 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.^{20c} The same three resonances were observed in spectra of MOF-808-0.65SO₄, albeit with different relative intensities. However, a new resonance appeared at 69 ppm in spectra of MOF-808-1.3SO₄ and MOF-808-2.5SO₄. Since the appearance of this new peak correlates with the observation of α -pinene conversion, the 69 ppm resonance was assigned to TMPO adsorbed on a strongly acidic site. In support of this assignment, exposure of MOF-808-2.5SO₄ to atmospheric moisture caused the 69 ppm resonance to

lose almost all of its intensity in the same way that MOF-808-2.5SO₄ loses its ability both to isomerize α -pinene and to display Hammett superacidity after exposure to atmospheric moisture.

In a preliminary survey of reactions, MOF-808-2.5SO₄ 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-808-2.5SO₄

Reaction Type	Substrates	Conversion
		5.6% ^a
Friedel-Crafts Acylation of Anisole		98% ^b
Esterification		100% ^c
Isomerization		80% ^d
		100% ^e

^a250 mg of MOF-808-2.5SO₄, 5 mL of anisole, 50 mg of benzoic acid, 110 °C, 12 h. ^b50 mg of MOF-808-2.5SO₄, 5 mL of anisole, 100 mg of benzoic anhydride, 110 °C, 12 h. ^c50 mg of MOF-808-2.5SO₄, 5 mL of anisole, 350 mg of 2-chlorobenzoyl chloride, 110 °C, 12 h. ^d200 mg of MOF-808-2.5SO₄, 10 mL of methanol, 1 g of oleic acid, 65 °C, 6 h. ^e150 mg of MOF-808-2.5SO₄, 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).²¹ 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, ³¹P MAS solid-state NMR spectra, and catalytic tests. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

yaghi@berkeley.edu
wklemper@uiuc.edu

Notes

The authors declare no competing financial interest.

^ΔVisiting scholar at University of California, Berkeley and Lawrence Berkeley National Laboratory.

ACKNOWLEDGMENTS

This research was partially supported by BASF SE (Ludwigshafen, Germany) and the U.S. Department of Defense, Defense Threat Reduction Agency Grant HDTRA 1-12-1-0053. We acknowledge Drs. H. Furukawa, K. Choi and Mr. Y. Zhao from the Yaghi group for their assistance in sorption and electron microscopy; Dr. C. Canlas (NMR spectroscopy facility, UC Berkeley) for his help in solid-state NMR experiments; Drs. W. L. Queen (Molecular Foundry, Lawrence Berkeley National Lab) and C. M. Brown (National Institute of Standards and Technology and University of Delaware) for discussions; and Drs. S. Teat and K. Gagnon for their assistance during the single-crystal diffraction data acquisition at the beamline 11.3.1 of the Advanced Light Source (ALS). Work at ALS was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. DOE under Contract No. DE-AC02-05CH11231. K.N. acknowledges financial support by Chevron Energy Technology Company, and the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geological and Biosciences of the US DOE (DE-AC02-05CH11231), and also financial support from the Basic Science Research Program through the National Research Foundation (NRF) in Korea funded by the Ministry of Education (2012R1A6A3A03039602).

REFERENCES

- (1) (a) Gillespie, R. J.; Peel, T. E. *Adv. Phys. Org. Chem.* **1971**, *9*, 1. (b) Gillespie, R. J.; Peel, T. E. *J. Am. Chem. Soc.* **1973**, *95*, 5173.
- (2) Hammett, L. P.; Deyrup, A. J. *J. Am. Chem. Soc.* **1932**, *54*, 2721.
- (3) Gold, V.; Laali, K.; Morris, K. P.; Zdunek, L. Z. *J. Chem. Soc., Chem. Commun.* **1981**, 769.
- (4) (a) Howells, R. D.; McCown, J. D. *Chem. Rev.* **1977**, *77*, 69. (b) Stang, P. J.; White, M. R. *Aldrichimica Acta* **1983**, *16*, 15.
- (5) (a) Yamaguchi, T. *Appl. Catal.* **1990**, *61*, 1. (b) Olah, G. A.; Prakash, G. K. S.; Molnár, A.; Sommer, J. *Superacid Chemistry*, 2nd ed.; John Wiley & Sons, Inc.: NJ, 2009; Chapters 2 and 5.
- (6) (a) Song, X.; Sayari, A. *Catal. Rev.-Sci. Eng.* **1996**, *38*, 329. (b) Arata, K. *Green Chem.* **2009**, *11*, 1719. (c) Yadav, G. D.; Nair, J. J. *Microporous Mesoporous Mater.* **1999**, *33*, 1. (d) Schmidt, F. *Appl. Catal., A* **2001**, *221*, 15.
- (7) Olah, G. A.; Kaspi, J.; Bukala, J. J. *Org. Chem.* **1977**, *42*, 4187.
- (8) (a) Mirodatos, C.; Barthomeuf, D. *J. Chem. Soc., Chem. Commun.* **1981**, 39. (b) Garralón, G.; Corma, A.; Fornés, V. *Zeolites* **1989**, *9*, 84.
- (9) (a) Arata, K. *Adv. Catal.* **1990**, *37*, 165. (b) Corma, A. *Chem. Rev.* **1995**, *95*, 559. (c) Okuhara, T. *Chem. Rev.* **2002**, *102*, 3641. (d) Arata, K.; Matsushashi, H.; Hino, M.; Nakamura, H. *Catal. Today* **2003**, *81*, 17.
- (10) (a) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013**, *341*, 974. (b) Gascon, J.; Corma, A.; Kapteijn, F.; Llabrés i Xmena, F. X. *ACS Catal.* **2014**, *4*, 361. (c) Yoon, M.; Srirambalaji, R.; Kim, K. *Chem. Rev.* **2012**, *112*, 1196. (d) Férey, G. *Chem. Soc. Rev.* **2008**, *37*, 191. (e) Sato, H.; Matsuda, R.; Sugimoto, K.; Takata, M.; Kitagawa, S. *Nat. Mater.* **2010**, *9*, 661. (f) Farrusseng, D.; Aguado, S.; Pinel, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 7502. (g) Bon, V.; Senkowska, I.; Weiss, M. S.; Kaskel, S. *CrystEngComm* **2013**, *15*, 9572. (h) Lee, J.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. *Chem. Soc. Rev.* **2009**, *38*, 1450. (i) Henke, S.; Schneemann, A.; Wütscher, A.; Fischer, R. A. *J. Am. Chem. Soc.* **2012**, *134*, 9464. (j) Ma, L.; Abney, C.; Lin, W. *Chem. Soc. Rev.* **2009**, *38*, 1248. (k) Zhang, Z.; Zhao, Y.; Gong, Q.; Li, Z.; Li, J. *Chem. Commun.* **2013**, *49*, 653. (l) Cao, S.; Gody, G.; Zhao, W.; Perrier, S.; Peng, X.; Ducati, C.; Zhao, D.; Cheetham, A. K. *Chem. Sci.* **2013**, *4*, 3573. (m) Jin, Z.; Zhao, H.-Y.; Zhao, X.-J.; Fang, Q.-R.; Long, J. R.; Zhu, G.-S. *Chem. Commun.* **2010**, *46*, 8612. (n) Li, T.; Kozłowski, M. T.; Doud, E. A.; Blakely, M. N.; Rosi, N. L. *J. Am. Chem. Soc.* **2013**, *135*, 11688.
- (11) (a) Akiyama, G.; Matsuda, R.; Sato, H.; Takata, M.; Kitagawa, S. *Adv. Mater.* **2011**, *23*, 3294. (b) Vimont, A.; Leclerc, H.; Maugé, F.; Daturi, M.; Lavalley, J.-C.; Surblé, S.; Serre, C.; Férey, G. *J. Phys. Chem. C* **2007**, *111*, 383. (c) Vermoortele, F.; Ameloot, R.; Alaerts, L.; Matthesen, R.; Carlier, B.; Ramos-Fernandez, E. V.; Gascon, J.; Kapteijn, F.; De Vos, D. E. *J. Mater. Chem.* **2012**, *22*, 10313. (d) Goesten, M. G.; Juan-Alcañiz, J.; Ramos-Fernandez, E. V.; Gupta, K. B. S. S.; Stavitski, E.; van Bekkum, H.; Gascon, J.; Kapteijn, F. *J. Catal.* **2011**, *281*, 177. (e) Akiyama, G.; Matsuda, R.; Sato, H.; Hori, A.; Takata, M.; Kitagawa, S. *Microporous Mesoporous Mater.* **2012**, *157*, 89. (f) Foo, M. L.; Horike, S.; Fukushima, T.; Hijikata, Y.; Kubota, Y.; Takata, M.; Kitagawa, S. *Dalton Trans.* **2012**, *41*, 13791. (g) Biswas, S.; Zhang, J.; Li, Z.; Liu, Y.-Y.; Grzywa, M.; Sun, L.; Volkmer, D.; Van Der Voort, P. *Dalton Trans.* **2013**, *42*, 4730. (h) Zang, Y.; Shi, J.; Zhang, F.; Zhong, Y.; Zhu, W. *Catal. Sci. Technol.* **2013**, *3*, 2044. (i) Vimont, A.; Goupil, J.-M.; Lavalley, J.-C.; Daturi, M.; Surblé, S.; Serre, C.; Millange, F.; Férey, G.; Audebrand, N. *J. Am. Chem. Soc.* **2006**, *128*, 3218. (j) Ponomareva, V. G.; Kovalenko, K. A.; Chupakhin, A. P.; Dybtsev, D. N.; Shutova, E. S.; Fedin, V. P. *J. Am. Chem. Soc.* **2012**, *134*, 15640.
- (12) Furukawa, H.; Gándara, F.; Zhang, Y.-B.; Jiang, J.; Queen, W. L.; Hudson, M. R.; Yaghi, O. M. *J. Am. Chem. Soc.* **2014**, *136*, 4369.
- (13) (a) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds: Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry*, 6th ed.; John Wiley & Sons, Inc.: NJ, 2009; p 84. (b) Adeeva, V.; de Haan, J. W.; Jänchen, J.; Lei, G. D.; Schünnemann, V.; van de Ven, L. J. M.; Sachtler, W. M. H.; van Santen, R. A. *J. Catal.* **1995**, *151*, 364. (c) Jin, T.; Yamaguchi, T.; Tanabe, K. *J. Phys. Chem.* **1986**, *90*, 4794.
- (14) Two crystallographically independent S atoms were located in the difference Fourier maps with a refined occupancy value of 0.2 and assigned to two sulfate ligands coordinating to the SBU with chelating and bridging modes. The uncoordinated O atoms for the former could be located but with high thermal displacement parameters, which were refined isotropically; the uncoordinated O atoms for the latter could not be located due to disorder. Nevertheless, an area of large residual electron density in the vicinity of this S atom was identified in the difference Fourier maps, which we attribute to the two remaining O atoms being dynamically and/or positionally disordered.
- (15) (a) Alaerts, L.; Séguin, E.; Poelman, H.; Thibault-Starzyk, F.; Jacobs, P. A.; De Vos, D. E. *Chem.—Eur. J.* **2006**, *12*, 7353. (b) Vermoortele, F.; Vandichel, M.; Van de Voorde, B.; Ameloot, R.; Waroquier, M.; Van Speybroeck, V.; De Vos, D. E. *Angew. Chem., Int. Ed.* **2012**, *51*, 4887. (c) Cirujano, F. G.; Llabrés i Xamena, F. X.; Corma, A. *Dalton Trans.* **2012**, *41*, 4249. (d) Vandichel, M.; Vermoortele, F.; Cottenie, S.; De Vos, D. E.; Waroquier, M.; Van Speybroeck, V. *J. Catal.* **2013**, *305*, 118. (e) Vermoortele, F.; Bueken, B.; Le Bars, G.; Van de Voorde, B.; Vandichel, M.; Houthoofd, K.; Vimont, A.; Daturi, M.; Waroquier, M.; Van Speybroeck, V.; Kirschhock, C.; De Vos, D. E. *J. Am. Chem. Soc.* **2013**, *135*, 11465.
- (16) (a) Comelli, N. A.; Ponzi, E. N.; Ponzi, M. I. *Chem. Eng. J.* **2006**, *117*, 93. (b) Ecormier, M. A.; Wilson, K.; Lee, A. F. *J. Catal.* **2003**, *215*, 57. (c) van der Waal, J. C.; van Bekkum, H.; Vital, J. M. *J. Mol. Catal. A* **1996**, *105*, 185. (d) Rachwalik, R.; Olejniczak, Z.; Jiao, J.; Huang, J.; Hunger, M.; Sulikowski, B. *J. Catal.* **2007**, *252*, 161.
- (17) (a) Walling, C. *J. Am. Chem. Soc.* **1950**, *72*, 1164. (b) Benesi, H. A. *J. Am. Chem. Soc.* **1956**, *78*, 5490. (c) Paul, M. A.; Long, F. A. *Chem. Rev.* **1957**, *57*, 1. (d) Tanabe, K.; Misono, M.; Ono, Y.; Hattori, H. *Stud. Surf. Sci. Catal.* **1989**, *51*, 5.
- (18) Umansky, B.; Engelhardt, J.; Hall, W. K. *J. Catal.* **1991**, *127*, 128.
- (19) (a) Hino, M.; Kobayashi, S.; Arata, K. *J. Am. Chem. Soc.* **1979**, *101*, 6439. (b) Hino, M.; Arata, K. *J. Chem. Soc., Chem. Commun.* **1980**, 851. (c) Yamaguchi, T.; Tanabe, K. *Mater. Chem. Phys.* **1987**, *16*, 67.
- (20) (a) Baltusis, L.; Frye, J. S.; Maciel, G. E. *J. Am. Chem. Soc.* **1986**, *108*, 7119. (b) Haw, J. F.; Zhang, J.; Shimizu, K.; Venkatraman, T. N.; Luigi, D.-P.; Song, W.; Barich, D. H.; Nicholas, J. B. *J. Am. Chem. Soc.* **2000**, *122*, 12561. (c) Zheng, A.; Huang, S.-J.; Liu, S.-B.; Deng, F. *Phys. Chem. Chem. Phys.* **2011**, *13*, 14889.
- (21) Na, K.; Musselwhite, N.; Cai, X.; Alayoglu, S.; Somorjai, G. A. *J. Phys. Chem. A* **2014**, DOI: 10.1021/jp501775q.