Supporting Information (33 pages)

Superacidity in Sulfated Metal-Organic Framework-808

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Section S1 Syntheses of Materials

Methods:

Chemicals and supplies. *N*,*N*-Dimethylformamide (DMF), anhydrous methanol and formic acid (purity > 98%) were obtained from EMD Millipore Chemicals; anhydrous acetone and anhydrous toluene were obtained from Acros Organics; zirconium oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$, purity ≥ 99.5%), benzoic acid (purity ≥ 99.5%), benzophenone (purity ≥ 99 %), oleic acid (analytical standard), methyl heptadecanoate (analytical standard), sulfuric acid (H_2SO_4, purity ≥ 95%), hydrofluoric acid (HF, 48 wt% in water), cyclopentane (purity ≥ 98%), anhydrous benzene, anhydrous ethyl acetate, anhydrous anisole, anhydrous dichloromethane, and anhydrous chloroform with amylenes as stabilizer were obtained from Sigma-Aldrich. 1,3,5-Benzenetricarboxylic acid (H_3BTC) was obtained from Aldrich. Trimethylphosphine oxide (TMPO) was obtained from Alfa Aesar. (±)-Citronellal (GC, purity ≥ 95%), (+)-isopulegol (purity ≥ 99%), (-)-isopulegol (purity ≥ 99%), alpha-pinene (purity ≥ 98%), camphene (purity ≥ 95%) , 4-methoxybenzophenone (purity ≥ 97%) and benzoic anhydride (purity ≥ 95%) were obtained from Aldrich. (*R*)-(+)-Limonene (analytical standard) and 2-chlorobenzoyl chloride (purity ≥ 97.0%) were obtained from Fluka.

Hammett Indicators: 4-Phenylazoaniline (analytical standard) and 2,4-dinitroaniline (analytical standard, 99.9%) were obtained from Fluka. 2-Nitroaniline (purity ≥ 98%), 4-nitrodiphenylamine (purity ≥ 99%), anthraquinone (purity ≥ 97%), and 4-nitrofluorobenzene (purity ≥ 99%) were obtained from Aldrich, 2,4-Dichloro-6-nitroaniline (purity > 98%) and 2-benzoylnaphthalene (purity ≥ 98%) were obtained from Alfa Aesar. 2-Bromo-4,6-dinitroaniline (purity ≥ 98.0%), 4-nitrotoluene (purity ≥ 99.0%), and 2,4-dinitrotoluene (purity ≥ 99.0%) were obtained from TCI. 2,4-Dinitrofluorobenzene (purity ≥ 99%) were obtained from Sigma.

All starting materials, reagents and solvents were used without further purification.

All glassware used to handle activated MOFs was dried at 120 ^{o}C for 12h and used immediately.

Analytical techniques. Single-crystal X-ray diffraction (SXRD) data were collected using synchrotron radiation in beamline 11.3.1 of the Advanced Light Source, Lawrence Berkeley National Laboratory (LBNL) (Supporting Information, SI, Section S2). Powder X-ray diffraction (PXRD) patterns were recorded using a Rigaku Miniflex 600 diffractometer (Bragg-Brentano geometry, Cu Kα radiation λ = 1.54056 Å) (SI, Section S3). Solution ^{1}H NMR spectra were acquired on a Bruker Avance-400 MHz NMR spectrometer. Carbon, hydrogen, nitrogen and sulfur elemental microanalyses (EA) were performed in the Microanalytical Laboratory of the College of Chemistry at UC Berkeley, using a Perkin Elmer 2400 Series II CHNS elemental analyzer. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was performed on a PerkinElmer Optical Emission Spectrometer Optima 7000DV instrument. Scanning electron microscope (SEM) images were obtained using a Zeiss Gemini Ultra-55 analytical scanning electron microscope with a working distance of 8.4 mm and a low acceleration voltages (5 keV) to avoid damage to the samples during observation. All MOF SEM samples were prepared by direct deposition of MOF/acetone dispersion (1 mg mL^{-1}) on the silicon substrate heated on a hot plate (60 °C) (SI, Section S4). Low-pressure gas (N_2 and Ar) adsorption isotherms were recorded on a Quantachrome Autosorb-1 volumetric gas adsorption analyzer. Liquid nitrogen and argon baths were used for the measurements at 77 and 87 K, respectively (SI, Section S5). Helium was used for the estimation of dead space for gas adsorption measurements. Ultra-high-purity grade N_2, Ar, and He gases (Praxair, 99.999% purity) were used throughout the adsorption experiments. Attenuated total reflectance (ATR) FTIR spectra of neat samples were performed on a Bruker ALPHA Platinum ATR-FTIR Spectrometer equipped with a single reflection diamond ATR module (SI, Section S6). Solid-state nuclear magnetic resonance (SSNMR) spectra

were acquired on a Bruker Avance-500 MHz NMR spectrometer using a standard Bruker double resonance magic angle-spinning (MAS) probe (SI, Section S8). Analyses of citronellal cyclization and alpha-pinene isomerization products were performed using a Shimadzu GCMS-QP2010 SE, gas chromatography-mass spectrometer (GC-MS) equipped with a SHRXI-5MS capillary column (30m, 0.25 mm i.d., 0.25 μm film thickness). The carrier gas was helium (flow rate = 1 mL/min) and the detector voltage was 0.25 kV. Diluted samples (1.0 μL) were injected manually in split mode with the split ratio of 20. Injector and detector temperatures were set at 250 and 200 °C, respectively. (SI, Section S9).

Synthesis and Characterization of MOFs:

General procedure for MOF formulation. Activated MOFs were analyzed using microanalyses (C, H, N, and S), ICP-OES analyses (Zr) and integrated solution ^{1}H NMR spectra of digested samples to determine their formula. A mixture containing 20 μL of DMSO-d_6 and 580 μL of hydrofluoric acid (48 wt% in water) was used to digest 10 mg of each MOF for NMR measurements. The formulation procedure used the formula $[Zr_6O_{10-x-2y}(OH)_{x+2y-2}(C_9H_3O_6)_2(HCOO)_x(SO_4)_y](H_2O)_z$ as a starting point. The value of x was determined using the ratio of integrated formate and trimesate resonances in the solution ^{1}H NMR spectrum of each digested sample. The value of y was determined from the results of C and S microanalyses. Finally, the value of z was determined by matching the calculated elemental microanalyses results with the found values.

Microcrystalline powder sample of MOF-808-P. Microcrystalline powder samples of MOF-808-P were prepared using slightly modified published procedures (*S1*). H_3BTC (2.1 g, 10 mmol) and $ZrOCl_2 \cdot 8H_2O$ (9.7 g, 30 mmol) were dissolved in DMF/formic acid (450 mL/450 mL) and placed in a 1-L screw-capped glass jar, which was heated to 130 °C for two days. A white precipitate was collected by filtration and washed three

times with 200 mL of fresh DMF. As-synthesized MOF-808-P was then immersed in 100 mL of anhydrous DMF for three days, during which time the DMF was replaced three times per day. The DMF-exchanged compound was filtrated off and immersed in 100 mL of water for three days, during which time the water was replaced three times per day. Water exchanged material was then immersed in 100 mL of anhydrous acetone for three days, during which time the acetone was replaced three times per day. The acetone-exchanged sample was then evacuated at room temperature for 24 h and at 150 °C for 24 h to yield activated sample (Yield: 5.1 g, 76 % based on Zr). ^{1}H solution NMR spectra of digested, activated sample (400 MHz, DMSO-d_6, ppm): 8.64 (s, BTC), 8.12 (s, *H*COOH), peak area ratio (BTC:*H*COOH) = 6.0:5.0. Anal. Calcd for $Zr_6C_{23}H_{18}O_{32}$ = $[Zr_6O_5(OH)_3(C_9H_3O_6)_2(HCOO)_5](H_2O)_2$: Zr, 40.43; C, 20.41; H, 1.34%. Found: Zr, 40.3; C, 21.02; H, 1.37%.

MOF-808-2.3SO$_4$ single crystal. Single crystals of MOF-808 were prepared following the reported procedure (*S1*). As-synthesized MOF-808 single crystals were immersed in anhydrous DMF for three days followed by water for three days, during which time the solvent was exchanged three times per day. Roughly 50 mg of water-exchanged MOF-808 crystals were immersed in 5 mL of 0.1 M sulfuric acid for 24 h during which time the mixture was stirred about once every two hours. The single crystals were then solvent exchanged with water for three days (water exchanged three times per day), quickly exchanged with anhydrous acetone for several times and immersed in anhydrous chloroform for three days during which time chloroform was exchanged three times per day. The chloroform in the solvent-exchanged crystals was removed under dynamic vacuum (30 mTorr) for 24 h at room temperature and 6 h at 80 °C. ^{1}H solution NMR spectra of digested, activated samples (400 MHz, DMSO-d_6, ppm): 8.64 (s, BTC), 8.12 (s, *H*COOH), peak area ratio (BTC:*H*COOH) = 6.0:0.04. Anal. Calcd for $Zr_6C_{18}H_{42.4}O_{16.2}S_{2.3}$ = $[Zr_6O_{5.6}(OH)_{2.4}(C_9H_3O_6)_2(SO_4)_{2.3}](H_2O)_{17}$: C, 13.35; H, 2.64; S, 4.55%. Found: C, 13.28; H, 2.61; S, 4.45%.

MOF-808-0.65SO_4 microcrystalline powder. Activated MOF-808-P microcrystalline powder (0.50 g, 0.37 mmol) was immersed in 50 mL of 0.005 M sulfuric acid (0.25 mmol) for 24 h during which time the mixture was stirred about once every two hours. The solution was then decanted and the remaining solid material was then solvent exchanged with 50 mL water for three days (water exchanged three times per day), quickly exchanged with 5 × 50 mL anhydrous acetone and immersed in 50 mL anhydrous chloroform for three days during which time chloroform was exchanged three times per day. The chloroform-exchanged material was activated under dynamic vacuum (30 mTorr) for 24 h at room temperature and 24 h at 150 °C to afford MOF-808-0.65SO_4 as white powder which was stored under Ar to avoid hydration (Yield: 0.49 g). ^{1}H solution NMR spectra of digested, activated sample (400 MHz, DMSO-d_6, ppm): 8.63 (s, BTC), 8.12 (s, *H*COOH), peak area ratio (BTC:*H*COOH) = 6.0:3.0. Anal. Calcd for $Zr_6C_{21}H_{13.3}O_{29.6}S_{0.65}$ = $[Zr_6O_{5.7}(OH)_{2.3}(C_9H_3O_6)_2(HCOO)_3(SO_4)_{0.65}](H_2O)$: Zr, 41.87; C, 19.29; H, 1.03; S, 1.59%. Found: Zr, 41.9; C, 19.91; H, 1.11; S, 1.40%.

MOF-808-1.3SO_4 microcrystalline powder. Activated MOF-808-P microcrystalline powder (0.50 g, 0.37 mmol) was immersed in 50 mL of 0.01 M sulfuric acid (0.5 mmol) for 24 h during which time the mixture was stirred about once every two hours. The solution was then decanted and the remaining solid material was then solvent exchanged with 50 mL water for three days (water exchanged three times per day), quickly exchanged with 5 × 50 mL anhydrous acetone and immersed in 50 mL anhydrous chloroform for three days during which time chloroform was exchanged three times per day. The chloroform-exchanged material was activated under dynamic vacuum (30 mTorr) for 24 h at room temperature and 24 h at 150 °C to afford MOF-808-1.3SO_4 as white powder which was stored under Ar to avoid hydration (Yield: 0.47 g). ^{1}H solution NMR spectra of digested, activated sample (400 MHz, DMSO-d_6, ppm): 8.63 (s, BTC), 8.12 (s, *H*COOH), peak area ratio (BTC:*H*COOH) = 6.0:1.8. Anal. Calcd for

$Zr_6C_{19.8}H_{10.2}O_{28.8}S_{1.3}$ = $[Zr_6O_{5.6}(OH)_{2.4}(C_9H_3O_6)_2(HCOO)_{1.8}(SO_4)_{1.3}]$: Zr, 42.18; C, 18.33; H, 0.79; S, 3.20%. Found: Zr, 41.8; C, 19.01; H, 0.96; S, 3.04%.

MOF-808-2.3SO_4 microcrystalline powder. Activated MOF-808-P microcrystalline powder (0.50 g, 0.37 mmol) was immersed in 50 mL of 0.05 M sulfuric acid (2.5 mmol) for 24 h during which time the mixture was stirred about once every two hours. The solution was then decanted and the remaining solid material was then solvent exchanged with 50 mL water for three days (water exchanged three times per day), quickly exchanged with 5 × 50 mL anhydrous acetone and immersed in 50 mL anhydrous chloroform for three days during which time chloroform was exchanged three times per day. The chloroform-exchanged material was activated under dynamic vacuum (30 mTorr) for 24 h at room temperature and 24 h at 150 °C to afford MOF-808-2.3SO_4 as white powder which was stored under Ar to avoid hydration (Yield: 0.48 g). ^{1}H solution NMR spectra of digested, activated sample (400 MHz, DMSO-d_6, ppm): 8.63 (s, BTC), 8.11 (s, *H*COOH), peak area ratio (BTC:*H*COOH) = 6.0:0.2. Anal. Calcd for $Zr_6C_{18.2}H_{13}O_{31.6}S_{2.3}$ = $[Zr_6O_{5.2}(OH)_{2.8}(C_9H_3O_6)_2(HCOO)_{0.2}(SO_4)_{2.3}](H_2O)_2$: Zr, 40.29; C, 16.09; H, 0.96; S, 5.43%. Found: Zr, 39.9; C, 16.69; H, 0.79; S, 5.47%.

MOF-808-2.5SO_4 microcrystalline powder. Activated MOF-808-P microcrystalline powder (0.50 g, 0.37 mmol) was immersed in 50 mL of 0.1 M sulfuric acid (5 mmol) for 24 h during which time the mixture was stirred about once every two hours. The solution was then decanted and the remaining solid material was then solvent exchanged with 50 mL water for three days (water exchanged three times per day), quickly exchanged with 5 × 50 mL anhydrous acetone and immersed in 50 mL anhydrous chloroform for three days during which time chloroform was exchanged three times per day. The chloroform-exchanged material was activated under dynamic vacuum (30 mTorr) for 24 h at room temperature and 24 h at 150 °C to afford MOF-808-2.5SO_4 as white powder which was stored under Ar to avoid hydration (Yield: 0.48 g). ^{1}H solution NMR spectra of digested, activated sample (400 MHz, DMSO-d_6, ppm): 8.63 (s, BTC), 8.12 (s,

*H*COOH), peak area ratio (BTC:*H*COOH) = 6.0:0.05. Anal. Calcd for $Zr_6C_{18}H_{14}O_{32.5}S_{2.5}$ = $[Zr_6O_5(OH)_3(C_9H_3O_6)_2(SO_4)_{2.5}](H_2O)_{2.5}$: Zr, 39.73; C, 15.69; H, 1.02; S, 5.82%. Found: Zr, 39.9; C, 15.85; H, 1.18; S, 5.62%.

Section S2 Single Crystal X-ray Diffraction Analyses

MOF-808-2.3SO_4 single crystal. A single crystal of partially activated MOF-808-2.3SO_4 was selected and mounted in a cryoloop. Diffraction data covering a sphere of the reciprocal space was collected on Bruker ApexII CCD detector using synchrotron radiation with λ = 0.7749 Å. Unit cell parameters were determined with a set of 300 reflections with $(I)/\sigma(I)$ >10. After data reduction and absorption correction, the structure was solved with direct methods as implemented in *ShelXS*. Full-matrix least-squares on F^2 were carried out using *ShelXL* and *OLEX2* (*S2*).

All framework atoms were located and refined anisotropically. Two independent positions were assigned to the μ_3 oxygen atoms, which correspond to either μ_3-O (O7 and O5) or μ_3-OH (O1 and O3) groups, consistent with our previous findings (*S1*). Their chemical occupancy was fixed to 0.5.

Two symmetrically independent positions, S1 and S2, were assigned to the sulfur atoms of the sulfate groups, and their chemical occupancy was first refined and then fixed to a value of 0.2.

An oxygen atom coordinated to the zirconium atoms in the SBU was disordered over two positions (O10 and O11) with partial occupancy of 0.5 for each position. This atom belongs to either one of the two sulfate groups or to a terminal ligand when the sulfate group is not present.

Two additional oxygen atoms, O8 and O15, were located, completing the sulfate group of S1. The occupancy values of these two atoms were fixed to be the same as the one of the corresponding sulfur atom. These oxygen atoms were refined isotropically. Anisotropic refinement resulted in large anisotropic displacement parameters (ADP), suggesting disorder. The bond distances and angles of the sulfur and oxygen atoms of this sulfate group are in the expected ranges.

In the case of the sulfate group corresponding to sulfur atom S2, only the position of

the oxygen atoms coordinating to the zirconium atoms could be located. However, an area of residual electron density was observed in the vicinity of the sulfur atom and at position expected for the missing oxygen atoms. Attempts to assign and refine the positions of these two oxygen atoms were unsuccessful, suggesting that this sulfate group exhibits disorder over several positions which could not be resolved due to low occupancies at these positions.

Finally, several areas of residual electron density were found inside the framework pores. Since the sample was not fully activated at 150 °C prior to the single crystal measurement, we attribute this electron density to organic solvent and/or water molecules that were left in the pores or were adsorbed during the sample mounting procedure which took place under ambient conditions.

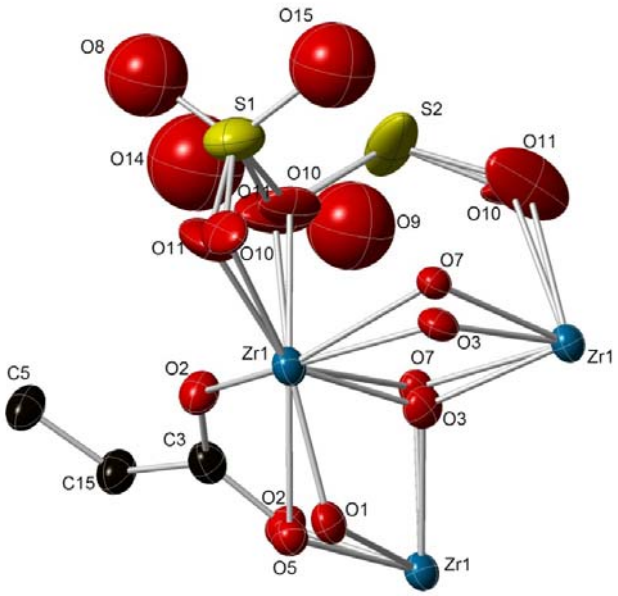


Figure S1. ORTEP representation (50% probability) showing more than the asymmetric unit of MOF-808-2.3SO_4.

Table S1. Crystal data and structure refinement for MOF-808-2.3SO_4 single crystal.

Identification code	MOF-808-2.3SO_4
Empirical formula	$C_{18}H_6O_{41.85}S_{2.40}Zr_6$
Formula weight	1516.09
Temperature/K	100.15
Crystal system	cubic
Space group	*Fd*-3*m*
a/Å	35.32 (2)
b/Å	35.32 (2)
c/Å	35.32 (2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	44078(63)
Z	16
$\rho_{calc/}$ mg mm^{-3}	0.914
Mu/mm^{-1}	0.817
F(000)	11635.0
Crystal size/mm^3	0.01 × 0.01 × 0.02
Radiation	Synchrotron (λ = 0.7749 Å)
2θ range for data collection	5.48 to 60.332°
Index ranges	-45 ≤ *h* ≤ 44, -45 ≤ *k* ≤ 45, -45 ≤ *l* ≤ 44
Reflections collected	97539
Independent reflections	2397 [R_{int} = 0.1869, R_{sigma} = 0.0393]
Data/restraints/parameters	2397/0/104
Goodness-of-fit on F^2	1.092
Final *R* indexes [*I*>=2σ (*I*)]	R_1 = 0.0512, wR_2 = 0.1501
Final *R* indexes [all data]	R_1 = 0.0763, wR_2 = 0.1662
Largest diff. peak/hole / e Å^{-3}	0.86/-0.67

Section S3 Powder X-ray Diffraction Patterns

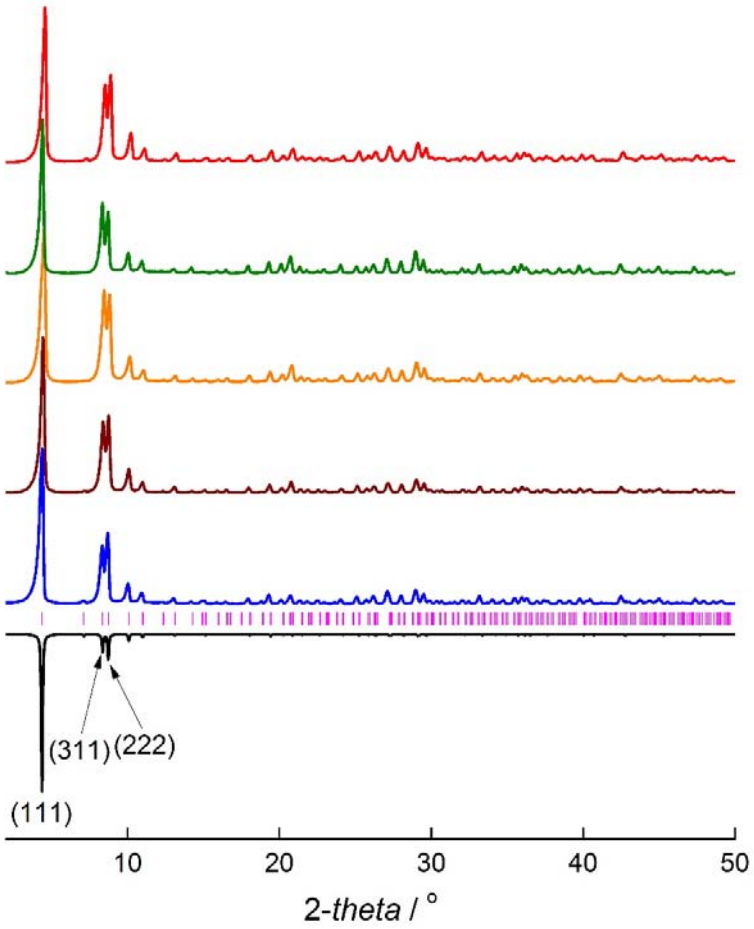


Figure S2. Experimental PXRD patterns of microcrystalline powder MOF-808-P (blue), MOF-808-0.65SO_4 (wine), MOF-808-1.3SO_4 (orange), MOF-808-2.3SO_4 (green), MOF-808-2.5SO_4 (red) and simulated pattern (black) from single-crystal X-ray data of MOF-808 (*S1*).

Section S4 Scanning Electron Microscopy

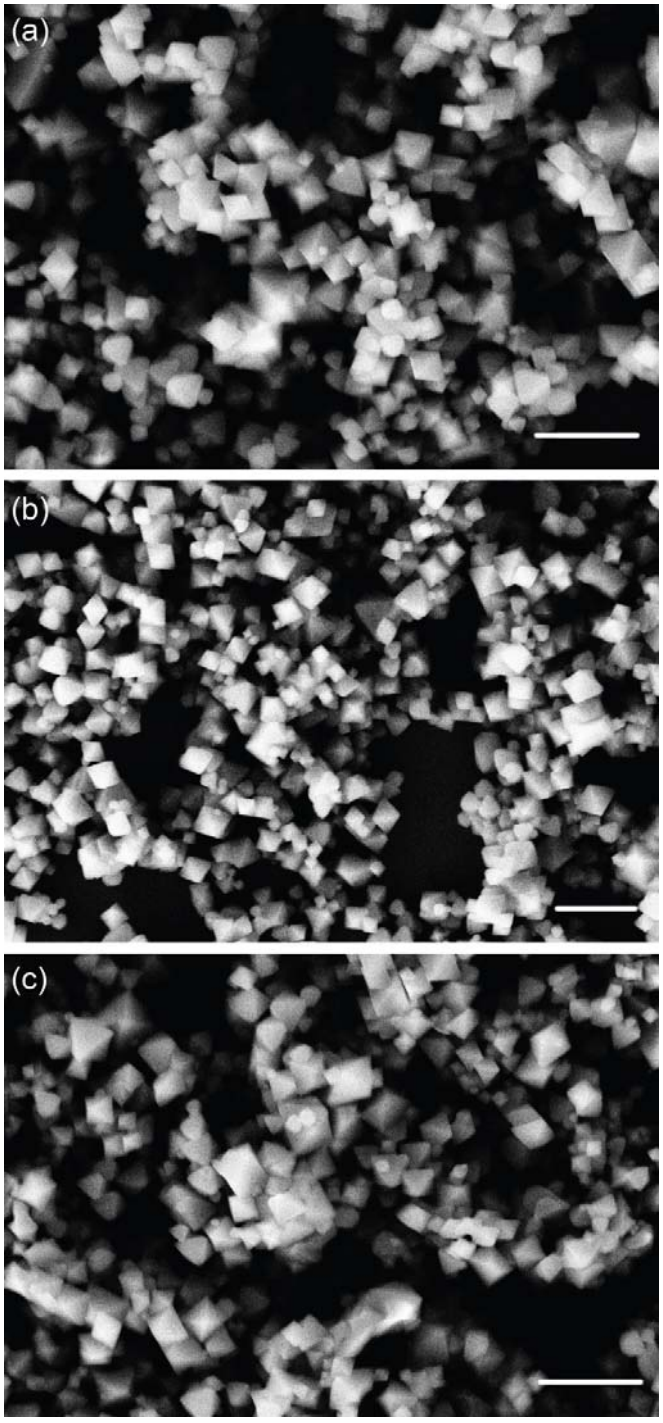


Figure S3. Scanning electron microscopy (SEM) images of MOF-808-0.65SO_4 (a), MOF-808-1.3SO_4 (b) and MOF-808-2.3SO_4 (c) (scale bar: 2 μm).

Section S5 N_2/Ar Adsorption Measurements

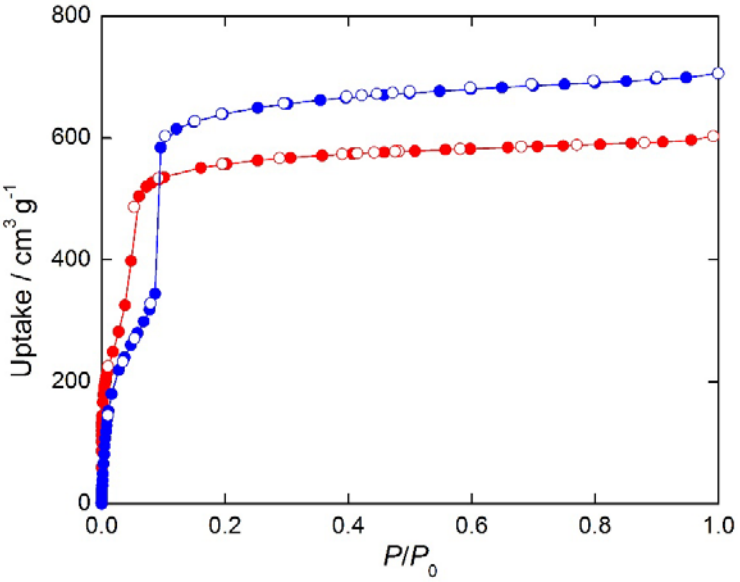


Figure S4. N_2 (red) and Ar (blue) isotherms of microcrystalline powder MOF-808-P at 77 K and 87 K, respectively.

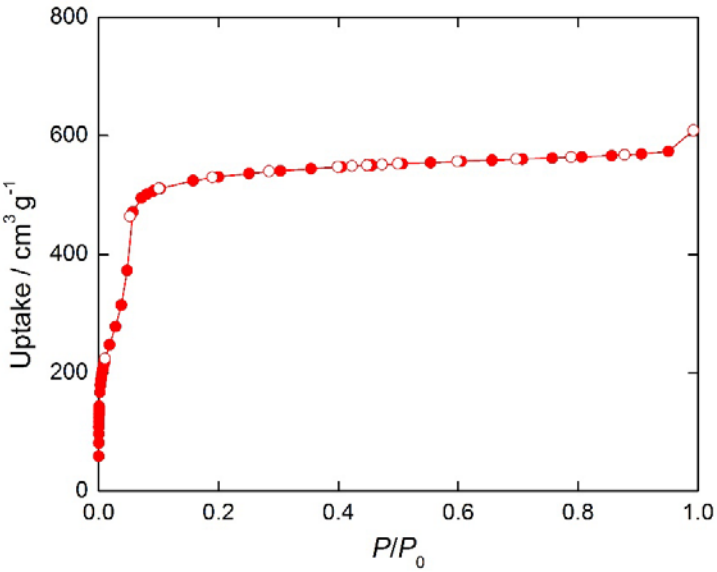


Figure S5. N_2 isotherm of microcrystalline powder MOF-808-0.65SO_4 at 77 K.

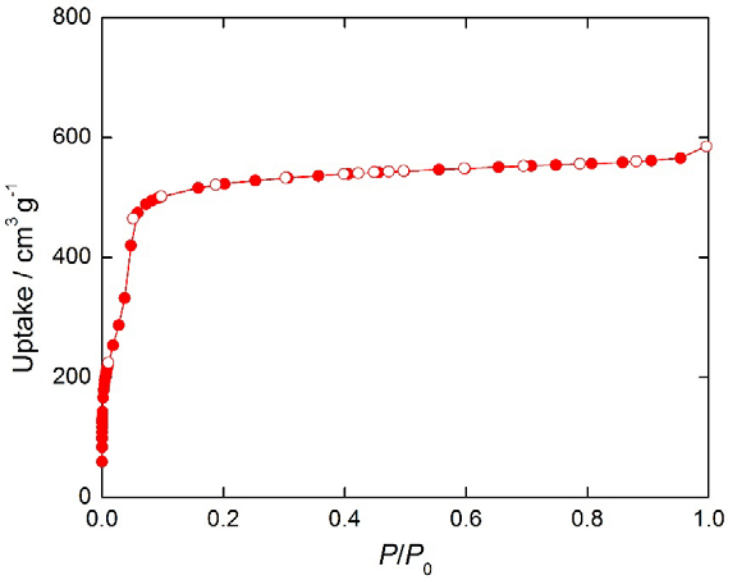


Figure S6. N_2 isotherm of microcrystalline powder MOF-808-1.3SO_4 at 77 K.

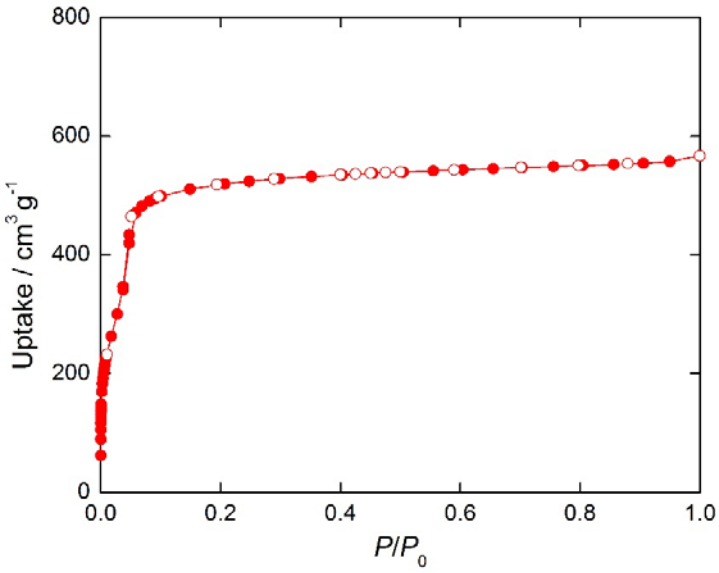


Figure S7. N_2 isotherm of microcrystalline powder MOF-808-2.3SO_4 at 77 K.

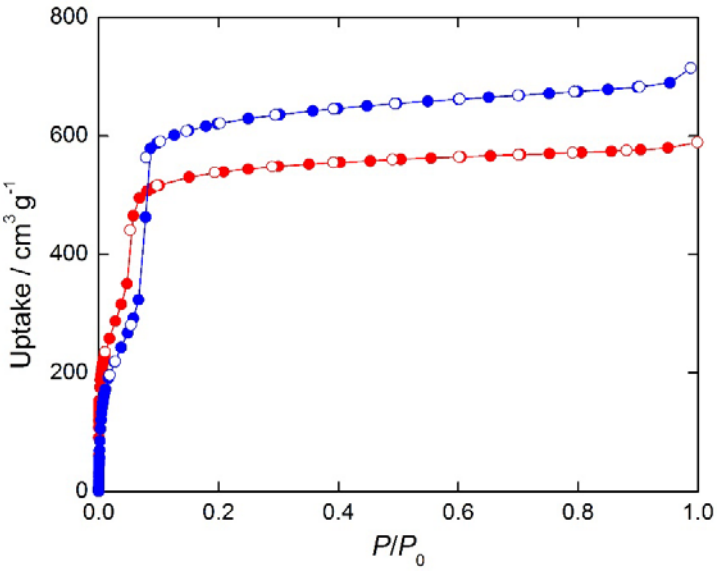


Figure S8. N_2 (red) and Ar (blue) isotherms of microcrystalline powder MOF-808-2.5SO_4 at 77 K and 87 K, respectively.

Section S6 Infrared Spectra

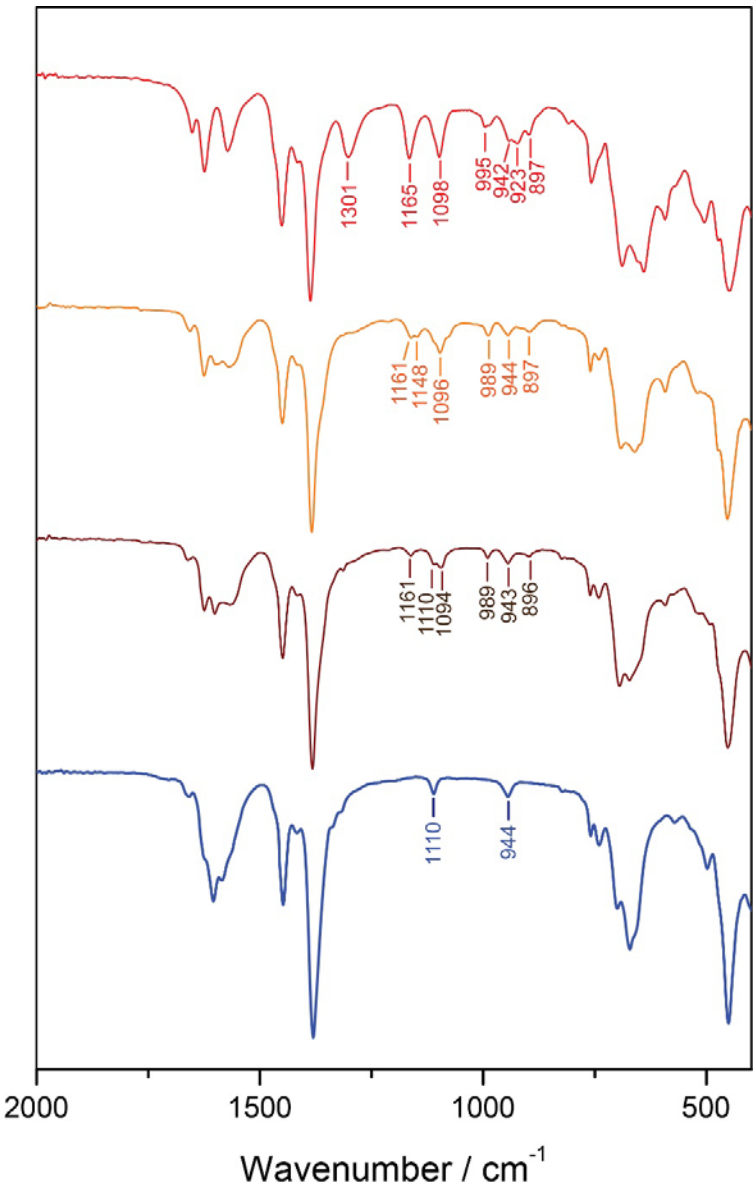


Figure S9. Infrared spectra of activated MOF-808-P (blue), MOF-808-0.65SO_4 (wine), MOF-808-1.3SO_4 (orange) and MOF-808-2.5SO_4 (red) recorded at room temperature, showing the range of 2000–400 cm^{-1}.

Section S7 Hammett Indicator Tests

A set of stock Hammett indicator solutions (0.5 wt%) was prepared in an inert atmosphere glovebox by dissolving Hammett indicators (Table S2) in anhydrous benzene. Hammett indicator stock solution (5 mL) was added to 20 mg of each activated MOF-808-*x*SO_4 sample in a 20-mL glass vial in the glovebox. The suspension was swirled every 30 mins, and after 4 h the color of the solid was then recorded (see Table S2).

Table S2. Hammett Indicators and Acidity of MOF-808-$x$$SO_4$ Measured by Hammett Indicator Tests.

Indicators	Color[a]		pK_a[a]	Hammett Indicator Tests[b]			
	Acid Form	Base Form		MOF-808-P	MOF-808-0.65SO_4	MOF-808-1.3SO_4	MOF-808-2.5SO_4
4-Phenylazoaniline	Red	Orange	+2.8	–	+	+	+
2-Nitroaniline	Red	Yellow	-0.2	–	+	+	+
4-Nitrodiphenylamine	Red	Yellow	-2.4	–	+	+	+
2,4-Dichloro-6-nitroaniline	Red	Yellow	-3.2	–	+	+	+
2,4-Dinitroaniline	Red	Yellow	-4.4	–	+	+	+
2-Benzoylnaphthalene	Yellow	Colorless	-5.9	–	–	+	+
2-Bromo-4,6-dinitroaniline	Red	Yellow	-6.6	–	–	+	+
Anthraquinone	Yellow	Colorless	-8.1	–	–	+	+
4-Nitrotoluene	Yellow	Colorless	-11.4	–	–	+	+
4-Nitrofluorobenzene	Yellow	Colorless	-12.4	–	–	+	+
2,4-Dinitrotoluene	Yellow	Colorless	-13.8	–	–	+	+
2,4-Dinitrofluorobenzene	Yellow	Colorless	-14.5	–	–	+	+

[a] See ref *S3*.

[b] Results of Hammett indicator tests are denoted as color change observed (+) and color change not observed (-).

Section S8 ^{31}P MAS NMR Characterizations

Sample preparation: About 200 mg of each MOF sample was placed in a Pyrex cell equipped with a stopcock. The sample was then outgassed under vacuum at 150 °C for 24 h, and 3.0 mL of 0.2 M trimethylphosphine oxide (TMPO) in dichloromethane was then added to the sample cell inside an inert atmosphere glovebox. After thoroughly mixing the TMPO solution and the MOF sample, the dichloromethane was removed under vacuum, first at room temperature for 24 h and then at 50 °C for 8 h. The sample was then transferred, inside the glovebox, into a 4 mm (o.d.) Bruker ZrO_2 NMR sample rotor with a gastight cap (*S4*).

Experimental parameters: Solid-state nuclear magnetic resonance (SSNMR) spectra were acquired on a Bruker Avance-500MHz NMR spectrometer using a standard Bruker double resonance magic angle-spinning (MAS) probe. The magic angle was adjusted by maximizing the number and amplitudes of the signals of the rotational echoes observed in the ^{79}Br MAS FID signal from KBr. The transmitter frequency was 202.46 MHz. High-power two-pulse phase modulation (TPPM) ^{1}H heteronuclear decoupling was applied for ^{31}P NMR data acquisition (*S5*). A 90^{o} ^{31}P pulse (6.75 μs) was used and the ^{1}H decoupling field corresponded to 30 kHz. The recycling delay between scans was 60s, and the sample spinning rate was 10 kHz. The ^{31}P chemical shifts were externally referenced to an 85% H_3PO_4 aqueous solution (as zero ppm).

Chemical shifts and relative intensities were calculated using the Gaussian deconvolution method (Bruker Topspin).

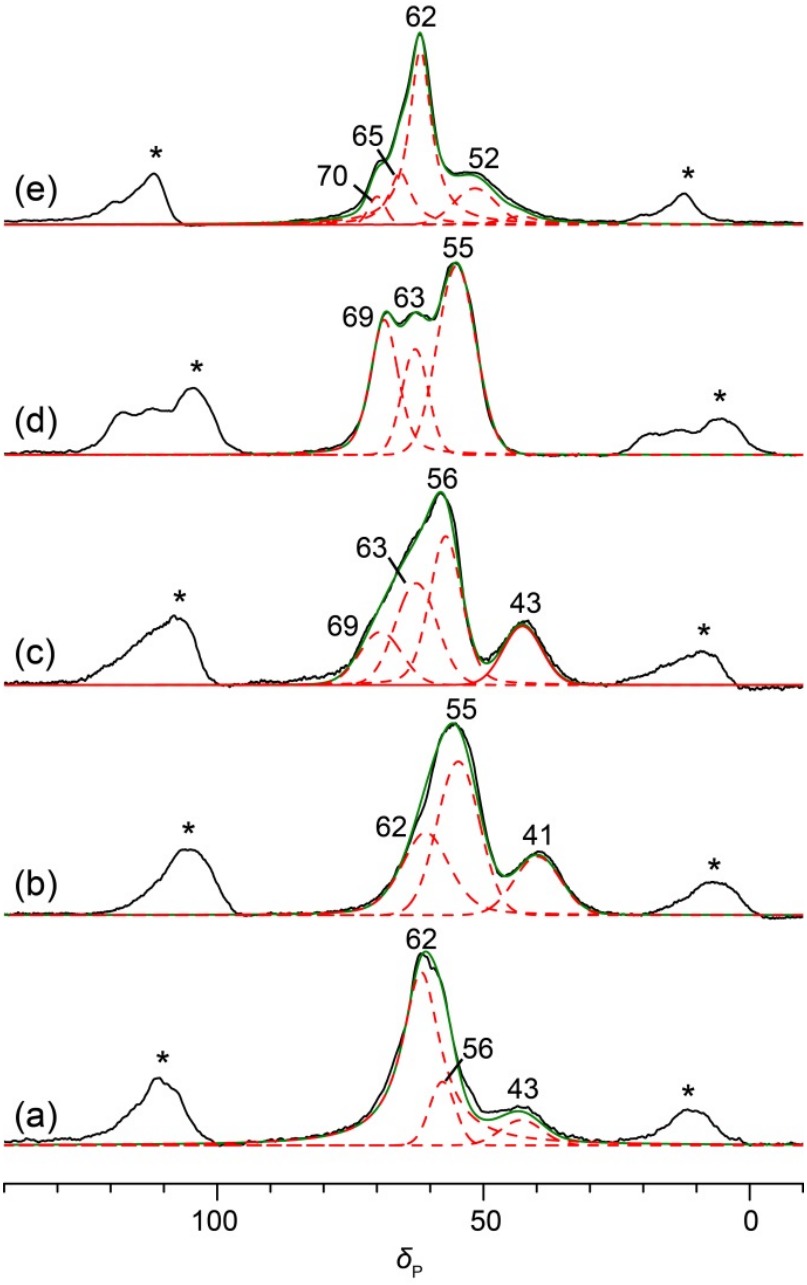
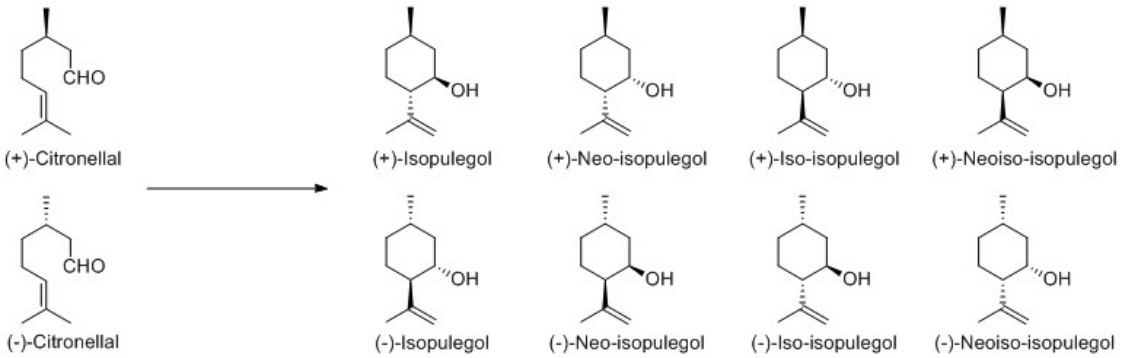


Figure S10. ^{31}P MAS NMR spectra of TMPO loaded on MOF-808-P (a), MOF-808-0.65SO_4 (b), MOF-808-1.3SO_4 (c), MOF-808-2.5SO_4 (d) and MOF-808-2.5SO_4 exposed to atmosphere moisture (e). Experimental spectra are shown in black, deconvoluted peaks in red dash, and the sum of the deconvoluted peaks in green. The asterisks denote spinning sidebands.

Section S9 Catalytic Test Reactions

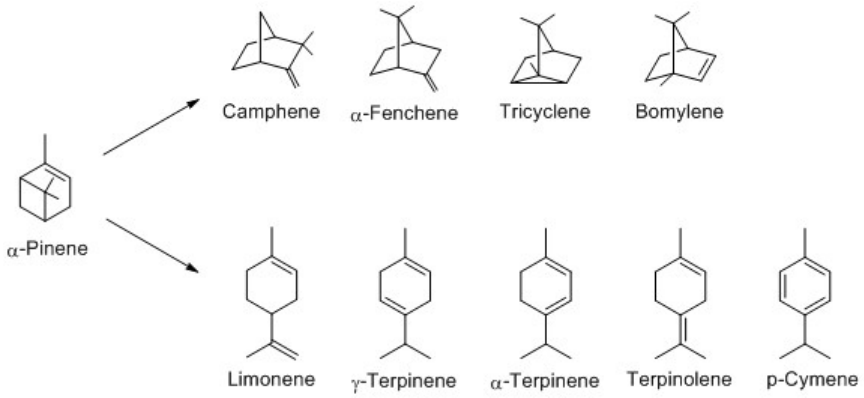


Scheme S1. Cyclization of (±)-citronellal to isopulegol isomers

Citronellal cyclization: The citronellal cyclization reactions were carried out in 15-mL Ace pressure tube (Sigma-Aldrich) loaded with 50 mg of activated catalysts. Each catalyst was first activated under dynamic vacuum at 150 °C for 24 h and stored in an inert atmosphere glovebox. After adding a solution of 1.5 mL (±)-citronellal in 5 mL toluene to the reactor (*c.a.* citronellal:Zr^{4+} mole ratio = 35) in the glovebox, the vessels were placed in an aluminum heating block at 60 ^{o}C with stirring. Reaction samples were removed in the dry box at different reaction times (0.5, 1, 1.5, 2, 3, 4, 5, 6, and 8 h), filtered through a 0.2 μm PTFE membrane filter, diluted 250 times with ethyl acetate and analyzed with a Shimadzu GCMS-QP2010 SE GC-MS, equipped with a SHRXI-5MS capillary column. Column temperature was initially 75 °C for 3 minutes, then gradually increased to 200 °C at 3 °C/min. Cyclohexanone was added as internal standard (*S6*), and calibration curves for (±)-citronellal and (±)-isopulegol were obtained using commercially available (±)-citronellal and (±)-isopulegol for quantification (*S7*). Conversions of (±)-citronellal at a given reaction time (Figure S11) were calculated by dividing the amount of (±)-citronellal left in the reaction mixture at that given reaction time (calculated using the calibration curve) over the initial amount of (±)-citronellal added. Selectivity towards (±)-isopulegol (Scheme S1) was calculated by dividing the

amount of (±)-isopulegol produced in the reaction mixture over the amount of the (±)-citronellal had been converted to that time.

Recyclability tests were performed on MOF-808-2.5SO_4 to test for catalyst stability. Here, the catalyst after the reaction was thoroughly washed by submerging it in anhydrous chloroform for one day, exchanging the solvent six times during the day, and dried under vacuum at 150 °C between consecutive runs (Figure S12). For filtration experiments to test for catalyst leaching, the reaction slurry was split in two parts after 0.5 h. While one part was left undisturbed, from the other part the catalyst was removed by filtration. The supernatant was allowed to react further in a separate reactor (Figure S12).



Scheme S2. Involved compounds in the alpha-pinene isomerization

alpha-Pinene isomerization: The alpha-pinene isomerization reactions were carried out in 4-mL Ace pressure tube (Sigma-Aldrich) loaded with 100 mg of activated catalysts. Each catalyst was first activated under dynamic vacuum at 150 °C for 24 h and stored in an inert atmosphere glovebox. After adding 3 mL of alpha-pinene to the reactor (*c.a.* pinene:Zr^{4+} mole ratio = 40) in glovebox, the vessels were placed in an aluminum heating block at 120 °C with stirring. Reaction samples were removed in the dry box at different reaction times (12, 24, 36, and 48 h), diluted 1000 times with ethyl acetate, filtered through a 0.2 μm PTFE membrane filter, and analyzed with a Shimadzu GCMS-QP2010

SE GC-MS, equipped with a SHRXI-5MS capillary column. Column temperature was initially 50 °C for 5 minutes, then gradually increased to 100 °C at 2 °C/min, and finally increased to 200 °C at 5 °C/min. Calibration curves for alpha-pinene, camphene and limonene were obtained using commercially available alpha-pinene, camphene and (*R*)-(+)-Limonene for quantification (*S7*). Conversions of alpha-pinene at a given reaction time (Figure S13) were calculated by dividing the amount of alpha-pinene left in the reaction mixture at that given reaction time (calculated using the calibration curve) over the initial amount of alpha-pinene added. Selectivity towards camphene and limonene (Scheme S2) was calculated by dividing the amount of camphene and limonene produced in the reaction mixture over the amount of the alpha-pinene had been converted to that time.

Recyclability tests were performed on MOF-808-2.5SO_4 to test for catalyst stability. Here, the catalyst after the reaction was thoroughly washed by submerging it in anhydrous chloroform for one day, exchanging the solvent six times during the day, and dried under vacuum at 150 °C between consecutive runs (Figure S14). For filtration experiments to test for catalyst leaching, the reaction slurry was split in two parts after 12 h. While one part was left undisturbed, from the other part the catalyst was removed by filtration. The supernatant was allowed to react further in a separate reactor (Figure S14).

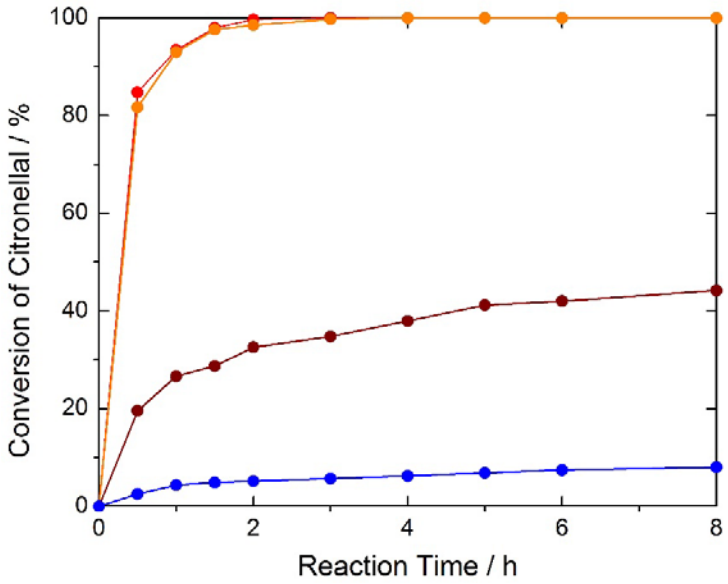


Figure S11. Conversion of (±)-citronellal over MOF-808-P (blue), MOF-808-0.65SO_4 (wine), MOF-808-1.3SO_4 (orange) and MOF-808-2.5SO_4 (red).

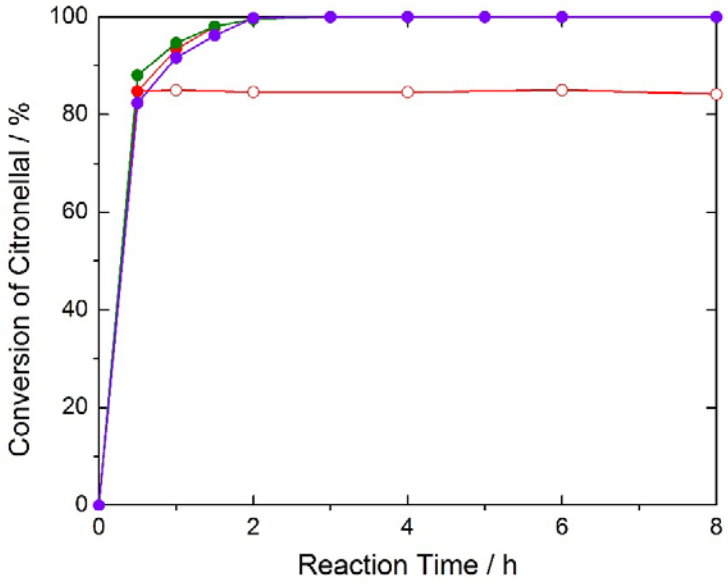


Figure S12. Recyclability test for MOF-808-2.5SO_4-catalyzed (±)-citronellal cyclization: run 1 (red solid), run 2 (olive), run 3 (violet). Filtration test for MOF-808-2.5SO_4-catalyzed (±)-citronellal cyclization: after 0.5 h in run 1, the reaction mixture was split in two parts and the catalysts was withdrawn from one sample (red hollow).

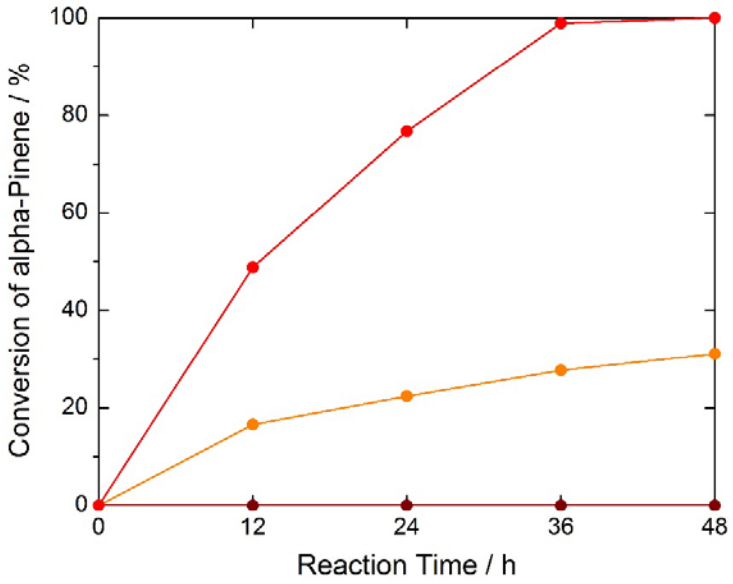


Figure S13. Conversion of alpha-pinene over MOF-808-P (blue, hidden under the wine curve), MOF-808-0.65SO_4 (wine), MOF-808-1.3SO_4 (orange) and MOF-808-2.5SO_4 (red).

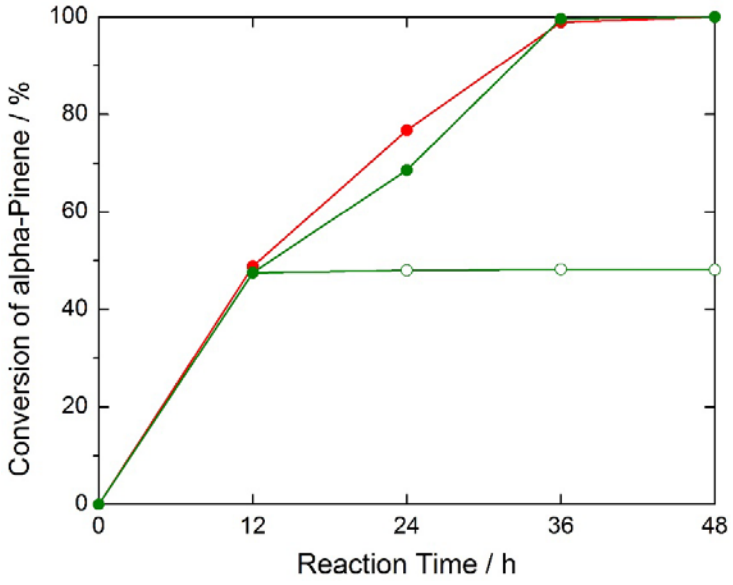
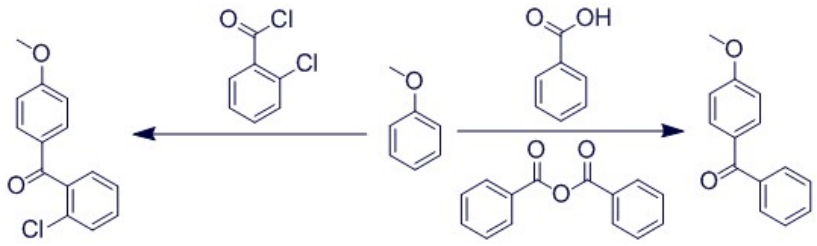
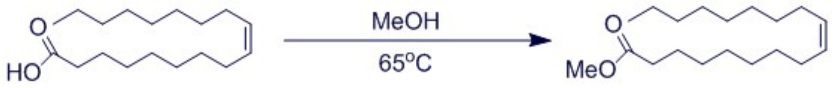


Figure S14. Recyclability test for MOF-808-2.5SO_4-catalyzed alpha-pinene isomerization: run 1 (red), run 2 (olive solid). Filtration test for MOF-808-2.5SO_4-catalyzed alpha-pinene isomerization: after 12 h in run 2, the reaction mixture was split in two parts and the catalysts was withdrawn from one sample (olive hollow).



Scheme S3. Friedel-Crafts acylation of anisole

Friedel-Crafts acylation of anisole: The Friedel-Crafts acylation of anisole (Scheme S3) was carried out in 15-mL Ace pressure tube (Sigma-Aldrich) loaded with 50 mg of activated catalysts (250 mg when using benzoic acid as the acylation reagent). Each catalyst was first activated under dynamic vacuum at 150 °C for 24 h and stored in an inert atmosphere glovebox. After adding a solution of acylation reagents in 5 mL anisole to the reactor in the glovebox (*c.a.* carboxylic acid:Zr^{4+} mole ratio = 0.4; carboxylic anhydride:Zr^{4+} mole ratio = 2; acyl chloride:Zr^{4+} mole ratio = 9), the vessels were placed in an aluminum heating block at 110 ^{o}C with stirring (180 ^{o}C when using benzoic acid as the acylation reagent). Reaction samples were removed after 12 h, filtered through a 0.2 μm PTFE membrane filter, diluted 20 times with ethyl acetate and analyzed with a Shimadzu GCMS-QP2010 SE GC-MS, equipped with a SHRXI-5MS capillary column. Column temperature was initially 40 °C for 1 minutes, then gradually increased to 300 °C at 10 °C/min. Benzophenone was added as internal standard (*S6*). Conversions of acylation reactions (Table 2) were calculated by dividing the amount of acylation reagents left in the reaction mixture over the initial amount added.



Scheme S4. Esterification of oleic acid with methanol

Esterification of oleic acid with methanol: The esterification of oleic acid with methanol (Scheme S4) was carried out in 15-mL Ace pressure tube (Sigma-Aldrich) loaded with 200 mg of activated catalysts. Each catalyst was first activated under dynamic vacuum at 150 °C for 24 h and stored in an inert atmosphere glovebox. After adding a solution of 1.0 g oleic acid in 10 mL anisole to the reactor in the glovebox (*c.a.* oleic acid:Zr^{4+} mole ratio = 4), the vessels were placed in an aluminum heating block at 65 ^{o}C with stirring. Reaction samples were removed in the dry box at different reaction times (1, 2, 3, 4, 5, and 6 h), filtered through a 0.2 μm PTFE membrane filter, diluted 250 times with methanol and analyzed with a Shimadzu GCMS-QP2010 SE GC-MS, equipped with a SHRXI-5MS capillary column. Column temperature was initially 75 °C for 1 minutes, then gradually increased to 300 °C at 10 °C/min. Methyl heptadecanoate was added as internal standard (*S6*). Calibration curves for oleic acid were obtained using commercially available oleic acid for quantification (*S7*). Conversions of oleic acid at a given reaction time (Figure S15) were calculated by dividing the amount of oleic acid left in the reaction mixture at that given reaction time (calculated using the calibration curve) over the initial amount of oleic acid added.

Recyclability tests were performed on MOF-808-2.5SO_4 to test for catalyst stability. Here, the catalyst after the reaction was quickly washed with 10 mL of anhydrous methanol followed by 6 × 10 mL of anhydrous chloroform, and dried under vacuum at 150 °C between consecutive runs (Figure S15). For control experiments, the reaction was stirred without catalysts or with same amount (200 mg) of activated MOF-808-P, and analyzed in the same manner (Figure S15).

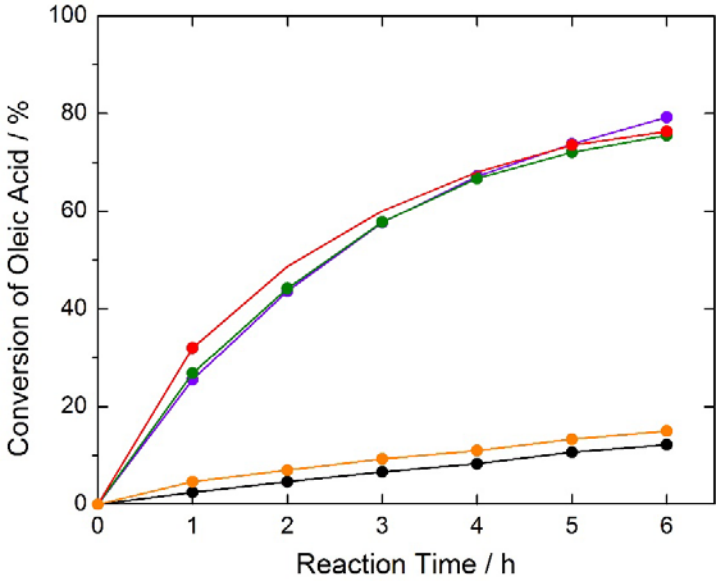
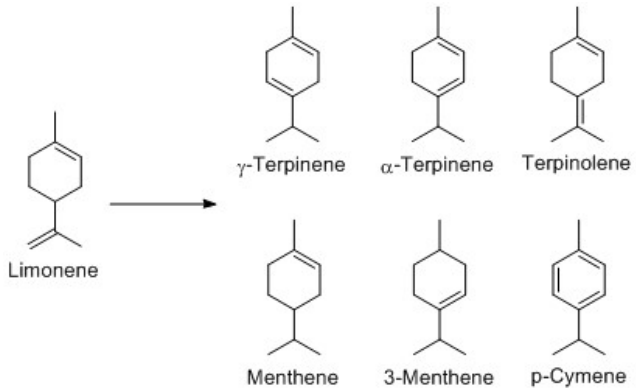


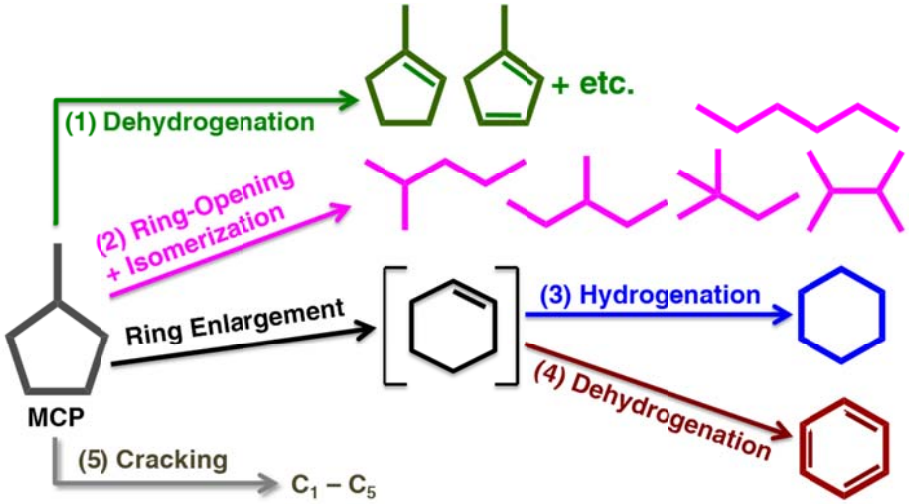
Figure S15. Recyclability test for MOF-808-2.5SO_4-catalyzed oleic acid esterification with methanol: run 1 (red), run 2 (olive), run 3 (violet). Control experiments for esterification of oleic acid and methanol with no catalysts added (black) and MOF-808-P added (orange).



Scheme S5. Involved compounds in limonene isomerization (*S8*)

Limonene isomerization: The limonene isomerization reactoin (Scheme S3) was carried out in 4-mL Ace pressure tube (Sigma-Aldrich) loaded with 150 mg of activated catalysts. Each catalyst was first activated under dynamic vacuum at 150 °C for 24 h and stored in an inert atmosphere glovebox. After adding 2.5 mL limonene to the reactor in the glovebox (*c.a.* limonene:Zr^{4+} mole ratio = 20), the vessels were placed in an aluminum heating block at 60 ^{o}C with stirring. Reaction samples were removed after 1 h, filtered through a 0.2 μm PTFE membrane filter, diluted 1000 times with ethyl acetate and analyzed with a Shimadzu GCMS-QP2010 SE GC-MS, equipped with a SHRXI-5MS capillary column. Column temperature was initially 50 °C for 5 minutes, then gradually increased to 100 °C at 2 °C/min, and finally increased to 200 °C at 5 °C/min. Calibration curves for limonene were obtained using commercially available (*R*)-(+)-Limonene for quantification (*S7*). Conversion of limonene (Table 2) was calculated by dividing the amount of limonene left in the reaction mixture (calculated using the calibration curve) over the initial amount of limonene added.

Methylcyclopentane conversion: Various hydrocarbon products can be obtained through gas-phase methylcyclopentane (MCP) conversion via typical catalytic reforming pathways such as cracking, dehydrogenation, ring-opening followed with isomerization, and ring-enlargement followed with hydrogenation or dehydrogenation (Scheme S6) (*S9*).



Scheme S6. Five reaction pathways of catalytic reforming of MCP, which are indicated by different numbers and colors. As the first pathway, MCP can be converted into the dehydrogenated version of MCP (1, green). Second pathway is ring-opening of MCP followed with isomerization to branched isomers as well as the linear isomer (2, pink). The C5-based cyclic ring of MCP can be further enlarged to C6-cyclic rings through hydrogenation (3, blue) or dehydrogenation (4, red) via cyclohexene intermediate species. The last reaction pathway is cracking (5, gray) to produce C1 ~ C5 based hydrocarbons. Among the five reaction pathways, no cracking was observed in the current study (Reprinted with permission from ref. *S9* (a). Copyright (2014) American Chemical Society).

The catalytic testing was performed using lab-built plug-flow reactor connected to a Hewlett Packard 5890 gas chromatograph (GC). A 10% SP-2100 on 100/120 Supelco port packed column in line with a FID detector was used to separate and analyze the C1 – C6 hydrocarbons. Mass flow controllers were carefully calibrated using a bubble flow meter and used to introduce the ultra-high purity (99.9999% Praxair) H_2 and He gases. Saturated vapor pressure of methylcyclopentane (MCP) was introduced to the reactor using a bubbler. The reactant flow was carefully calibrated at different temperatures and partial pressures of

He carrier. A total flow of 40 mL/min was used. Partial pressure of reactant was calculated by using the known temperature vs. saturated vapor pressure plots and was 50 Torr with 5:1 H_2 excess. 50 – 100 mg charges of the catalysts were diluted by quartz sand loaded in the reactor bed. The activated catalysts were reduced at 150 - 200 °C for 2 h under a flow of 210 Torr H_2 in 550 Torr He prior to catalytic testing. The catalytic activity and selectivity were evaluated for total MCP conversions around 3% (Table S3).

Table S3. Mass activity and product selectivity of MOF-808-P and MOF-808-2.5SO_4 to various products on methylcyclopentane conversion

Catalyst	Mass Activity (mmol/h/g catalyst)[a]	Selectivity (%)			
		Dehydrogenation	Isomerization	Cyclohexane	Benzene
MOF-808-2.5SO_4	0.11	61.4	38.6	0	0
MOF-808-P	No activity	N/A	N/A	N/A	N/A

[a] Mass activity, defined as the amount of methylcyclopentane converted (mmol) per given reaction time (h) and catalyst mass (g).

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Section S10 References

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