

Supporting Information for

Sulfate-Functionalized Metal–Organic Frameworks Supporting Pd Nanoparticles for the Hydrogenolysis of Glycerol to 1,2-propanediol

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Section S1. Characterization Methods

^1H NMR analysis was recorded on a Bruker NMR 500 DRX spectrometer at 500 MHz and referenced to the proton resonance resulting from incomplete deuteration of $\text{DMSO-}d_6$ ($\delta = 2.50$). Infrared spectra (IR) were recorded on a Nicolet 6700 FTIR spectrometer equipped with an MCT detector using ATR mode. Thermogravimetric analysis (TGA) was performed in air using a SDT Q600 Synchronous thermal analyzer equipped with an Alumina pan. Inductively coupled plasma-optical emission spectrometry (ICP-OES) analyses were performed on an Agilent ICP-OES instrument. Samples were diluted in 5% HNO_3 matrix and analyzed with a ^{159}Tb internal standard against a six-point standard curve over the range from 1 ppm to 100 ppm. The correlation coefficient was >0.9997 for all analytes of interest. Ion spectroscopy was performed on a Metrohm 930 ion spectroscopy. Powder X-ray diffraction (PXRD) was carried out on a Japan Rigaku DMax- γ A rotating anode X-ray diffractometer equipped with graphite monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). Nitrogen sorption measurements were conducted using a Micromeritics ASAP 2460 system at 77 K. The samples were prepared at 150 °C in vacuum for 10 h. The surface area was calculated using Brunauer-Emmett-Teller (BET) method in the range of $P/P_0 = 0.05\text{-}0.3$. Microporous surface areas, pore volumes, and mean pore diameters of micropores were evaluated by the HK method from the adsorption branches of isotherms. Transmission electron microscopy (TEM) and EDX mapping were performed on Phillips Analytical FEI Tecnai F30 electron microscope operated at an electron acceleration voltage of 300 kV. The samples were suspended in ethanol solvent and the specimens are sample powders deposited onto a Cu microgrid coated with a holey carbon film for EDX-mapping. GC-MS spectral analyses were performed on a Shimadzu GCMS-QP2010 Plus equipped with SH-Rxi-5Sil MS 30 m \times 0.5 mm \times 0.25 μm column. Ammonia-Temperature-programmed desorption (NH_3 -TPD) measurements were obtained using a Micromeritics AutoChem II 2920 instrument. The samples were preheated at 200 °C for 1 h to clean the surface of the sample from moisture and other adsorbed gas. After that, the sample was cooled down to 60 °C and then equilibrated in a 10 vol% NH_3/He stream for 1 h, followed by flushing in Ar for 30 min to remove any physisorbed molecules. The NH_3 -TPD experiment was then operated at 60-500 °C with a heating rate of 10 °C min^{-1} and holding at 500 °C for 1 h. The signal of the desorbed NH_3 was monitored by an on-line quadrupole mass spectrometer ($m/z = 16$).

Section S2. Characterization of Catalysts

Analysis of the composition of MOF-808 by ^1H NMR.

To determine the ratio of the capping formates to BTC, 2 mg of MOF-808 was digested in 50 μL D_3PO_4 , then 50 μL D_2O and 300 μL $\text{DMSO-}d_6$ were added to the digested solution. The sample was then analyzed by ^1H NMR and the ratio of BTC ligand and formate was approximately 1:1 as determined by the integrations corresponding to each ligand (Figure S1). The ratio of BTC and Zr was 1/3 determined by TGA analysis. We thus deduced a formula for MOF-808 as $\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{BTC})_2(\text{HCO}_2)_6$, considering the molar ratio of $\text{Zr}/\text{BTC}/\text{HCO}_2^- = 3/1/3$.

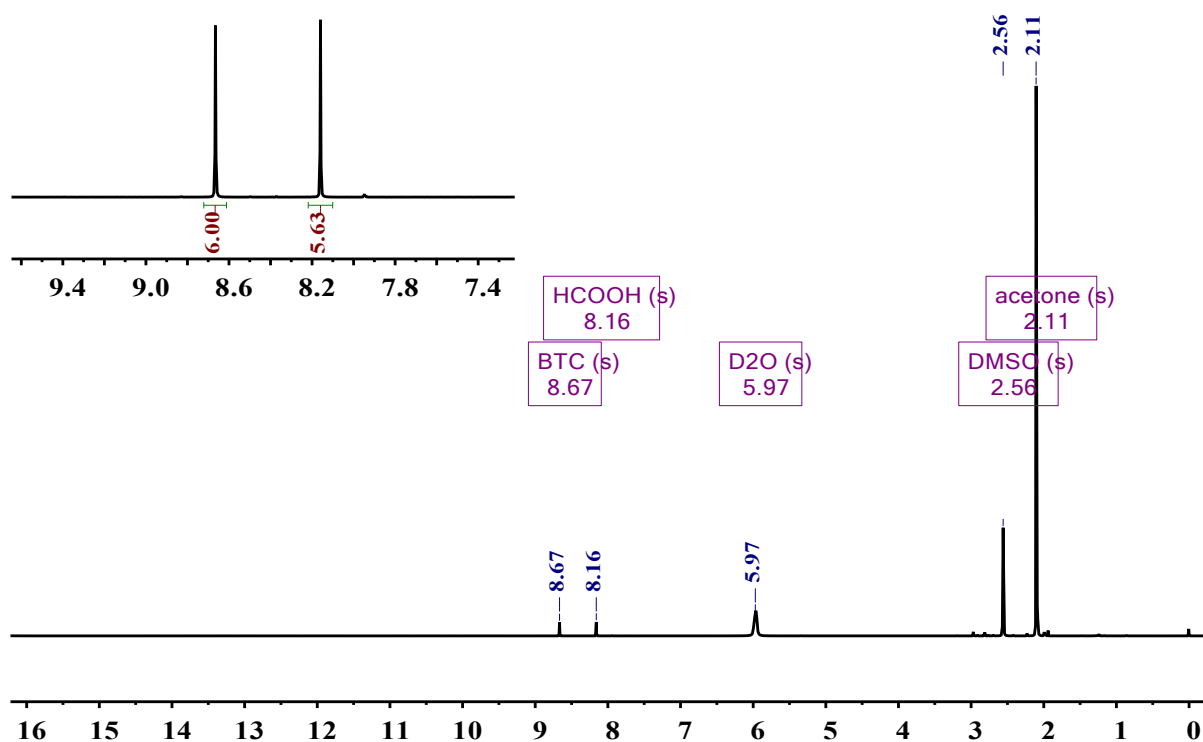


Figure S1. ^1H NMR spectrum of MOF-808 digested in $\text{D}_3\text{PO}_4/\text{D}_2\text{O}/\text{DMSO-}d_6$.

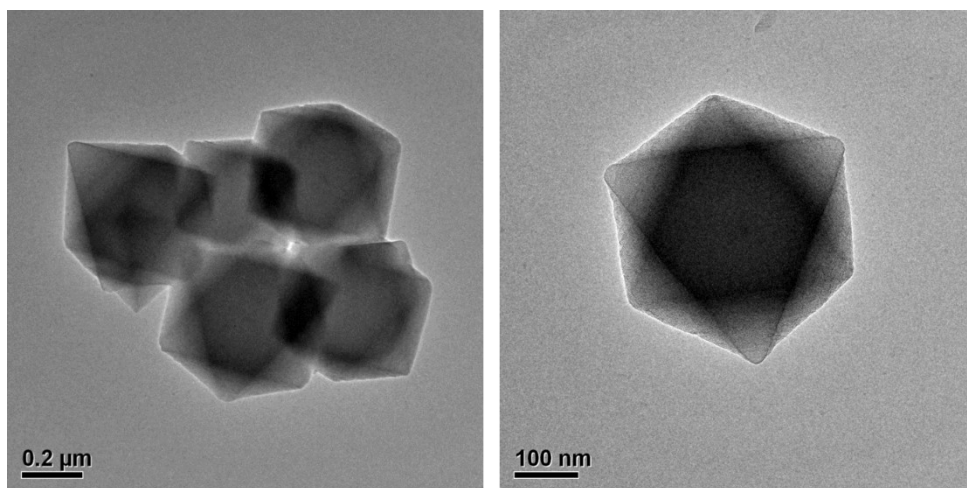


Figure S2. TEM images of MOF-808.

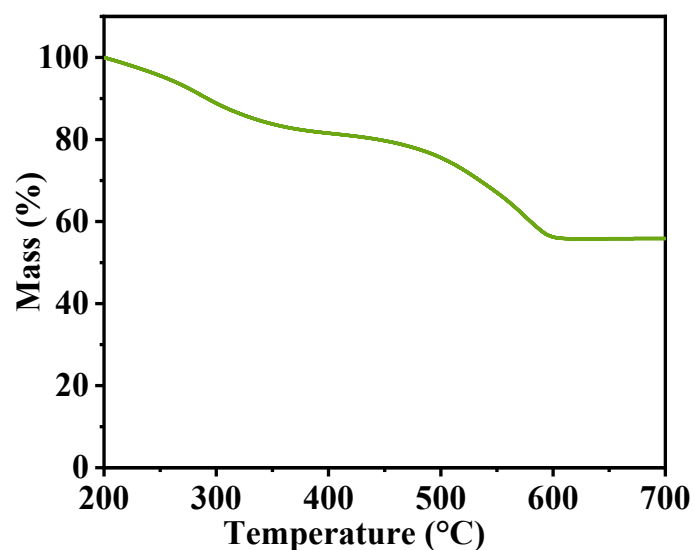


Figure S3. TGA curve of MOF-808 in the 200 - 700 °C range.

Analysis of the composition of MOF-808-SO₄ by ¹H NMR.

MOF-808-SO₄ was analyzed by ¹H NMR and the ratio of BTC ligand and formate was approximately 124:1 as determined by the integrations corresponding to each ligand (Figure S4). The molar ratio Zr/BTC/HCO₂⁻ = 6/2/0.05. That's to say, there was 0.05 HCO₂H in every Zr₆ cluster, the HCO₂H was almost completely replaced by SO₄ and OH/H₂O groups.

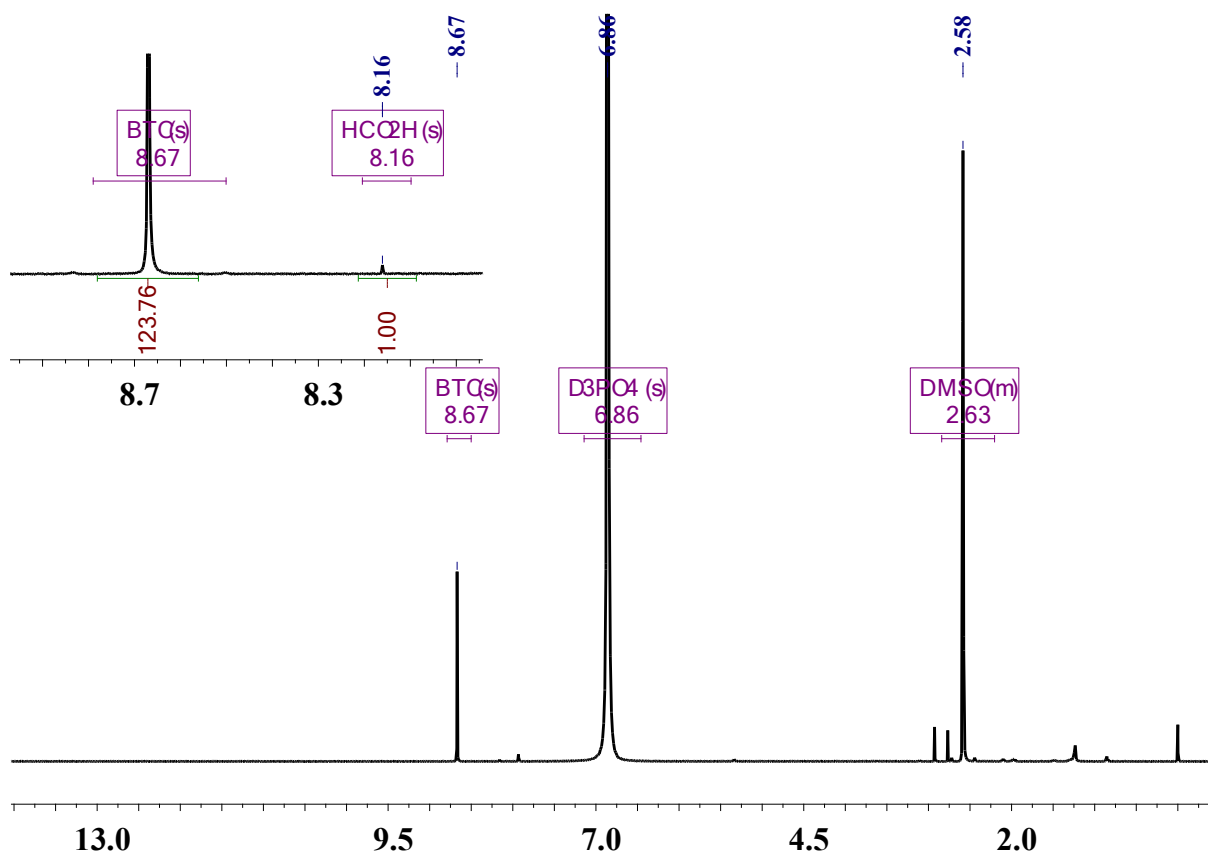


Figure S4. ^1H NMR spectrum of MOF-808-SO₄ digested in D₃PO₄/D₂O/DMSO-*d*₆.

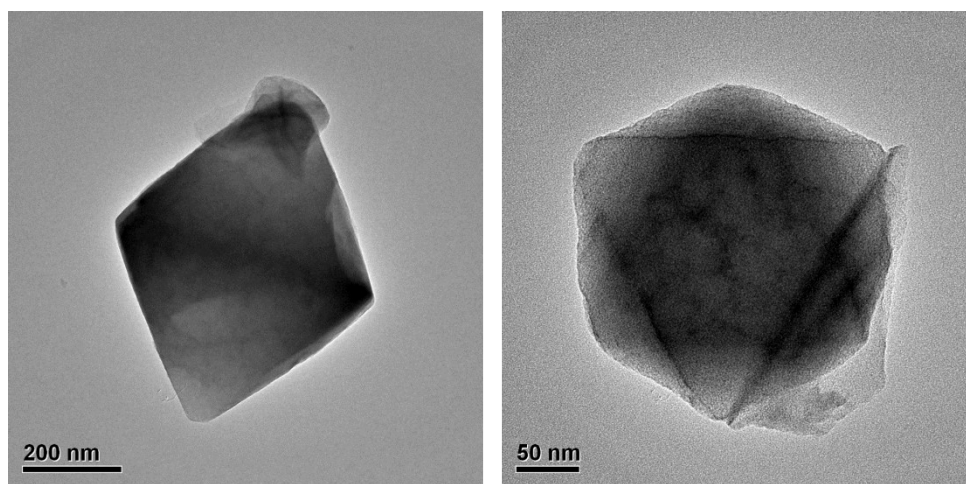


Figure S5. TEM images of MOF-808-SO₄.

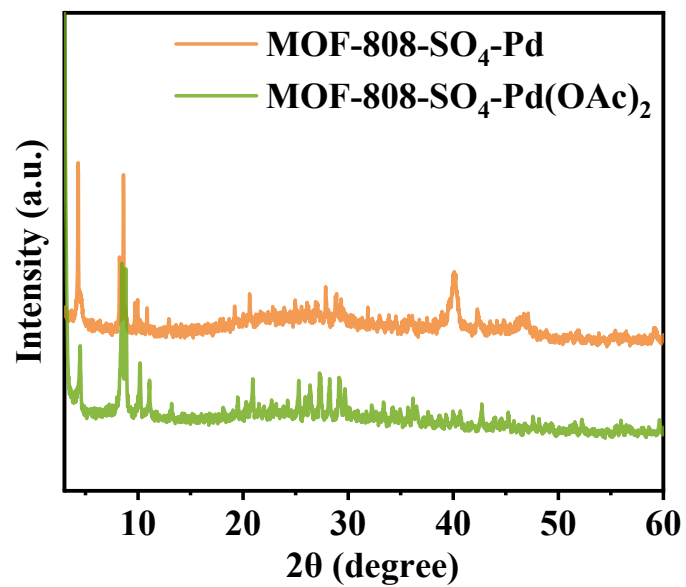


Figure S6. PXRD patterns of MOF-808-SO₄-Pd(OAc)₂ and MOF-808-SO₄-Pd.

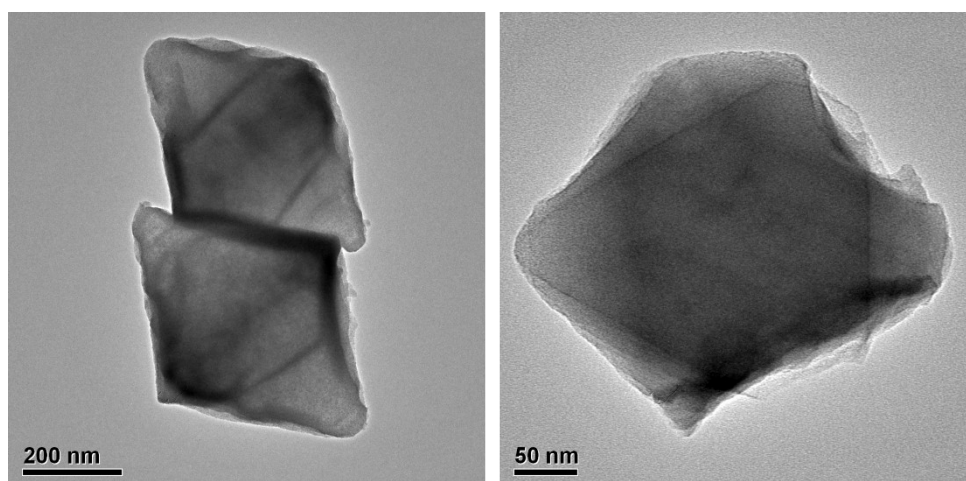


Figure S7. TEM images of MOF-808-SO₄-Pd(OAc)₂.

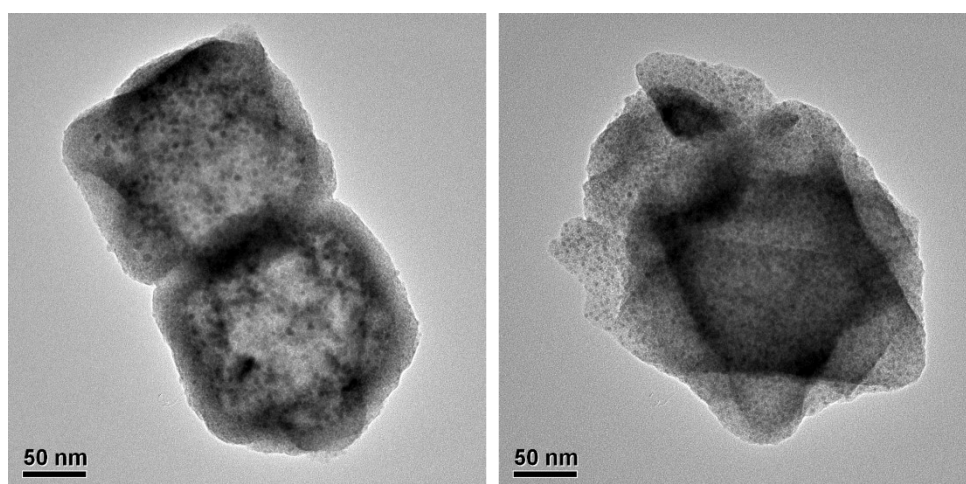


Figure S8. TEM images of MOF-808-SO₄-Pd.

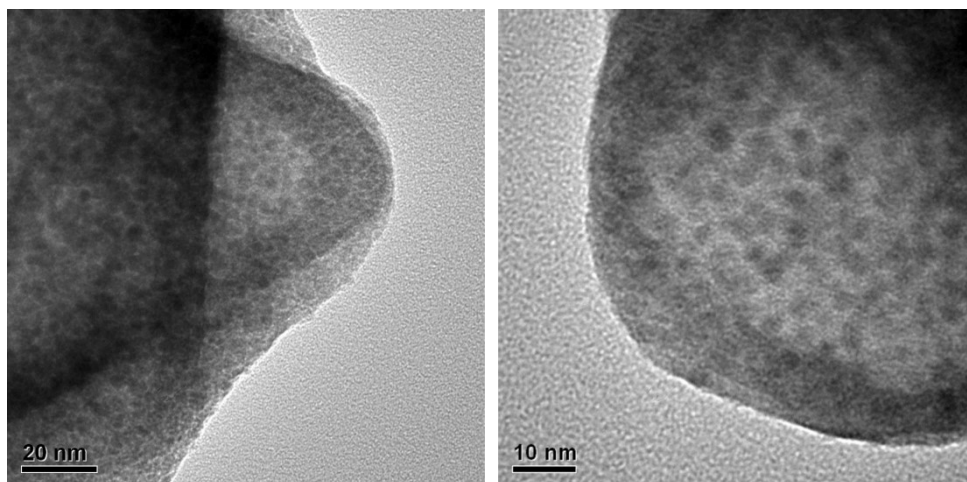


Figure S9. High resolution TEM images of MOF-808-SO₄-Pd.

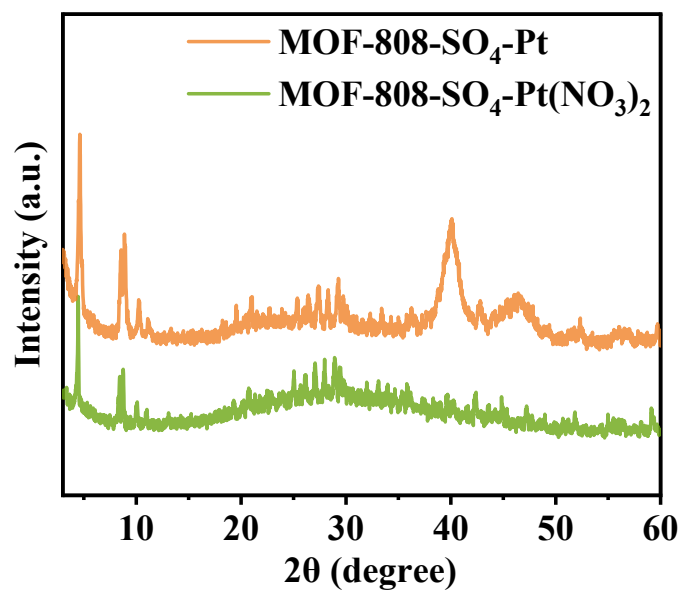


Figure S10. PXRD patterns of MOF-808-SO₄-Pt(NO₃)₂ and MOF-808-SO₄-Pt.

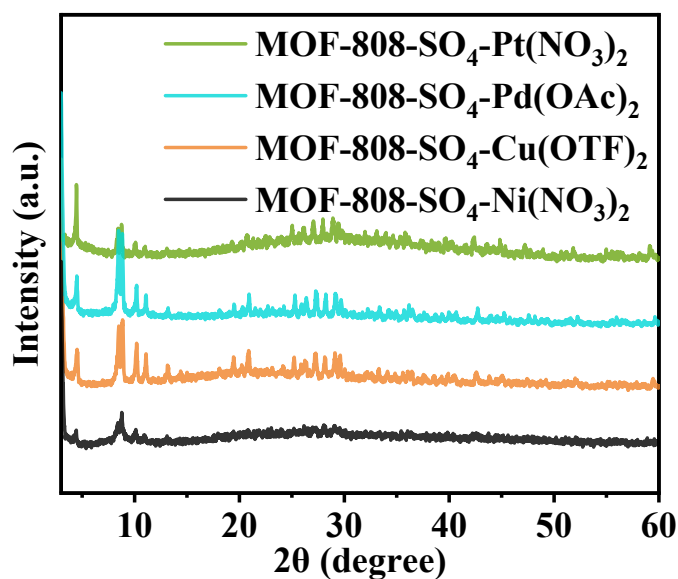


Figure S11. PXRD patterns of MOF-808-SO₄-M²⁺.

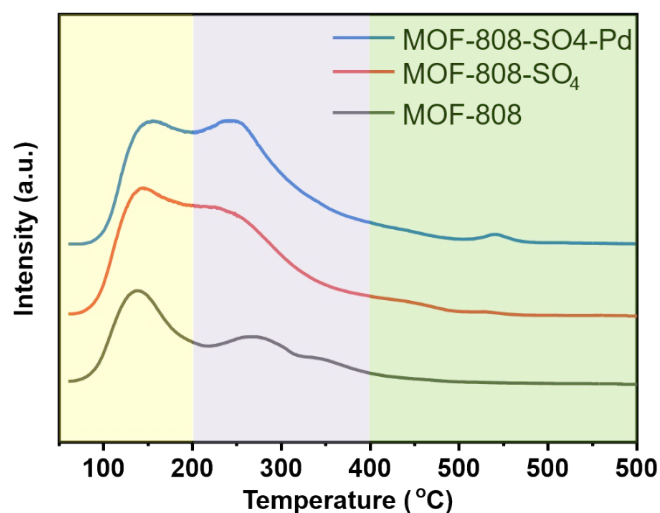


Figure S12. NH₃-TPD profiles of MOF-808, MOF-808-SO₄ and MOF-808-SO₄-Pd in the temperature range of 60 – 500 °C.

The acidities were estimated by NH₃-TPD in Figure S12, and the strength of the acid sites was determined by the temperature of NH₃ desorption. According to literature, we divided the NH₃ desorption into three temperature ranges: weak acid sites (below 200 °C), medium strong acid sites (200 – 400 °C), and strong acid sites (above 400 °C).¹ These three samples all have obvious NH₃ desorption behavior at the weak acid sites and the medium strong acid sites. We attributed the desorption peaks at around 150 °C to the Lewis acidic Zr⁴⁺ sites, and the peaks at around 250 °C to Brønsted acid site.

Synthesis and Characterization of MOF-801, MOF-801-SO₄ and MOF-801-SO₄-Pd

Synthesis of MOF-801. MOF-801 was synthesized according to a procedure published earlier.² Briefly, ZrCl₄ (2.585 mmol, 1 eq.) was dissolved in 50 mL water. Then, formic acid (258.5 mmol, 100 eq.) as a modulator and fumaric acid (7.75 mmol, 3 eq.) as a linker molecule were added to the solution of the metal precursor. The reaction mixture was transferred into a Teflon-lined pressure vessel and heated at 120 °C for 24 h. A white precipitate was collected by centrifugation and washed with water and acetone. Finally, the product was dried overnight at 100 °C.

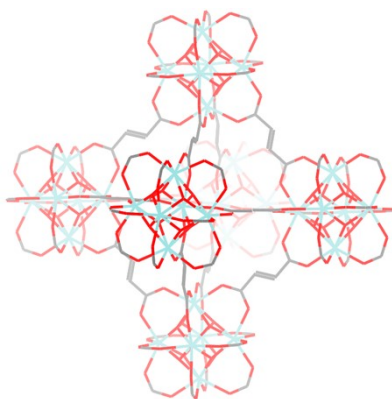


Figure S13. Structure of MOF-801.

The sample was then analyzed by ¹H NMR and the ratio of fumaric acid ligand and formate was approximately 4.7:1 as determined by the integrations corresponding to each ligand (Figure S16). Thus the formula for MOF-801 as Zr₆(μ₃-O)₄(μ₃-OH)₄(fumaric acid)_{4.95}(HCO₂)_{2.11}, considering the molar ratio of Zr/fumaric acid/HCO₂⁻ = 6/4.95/2.11.

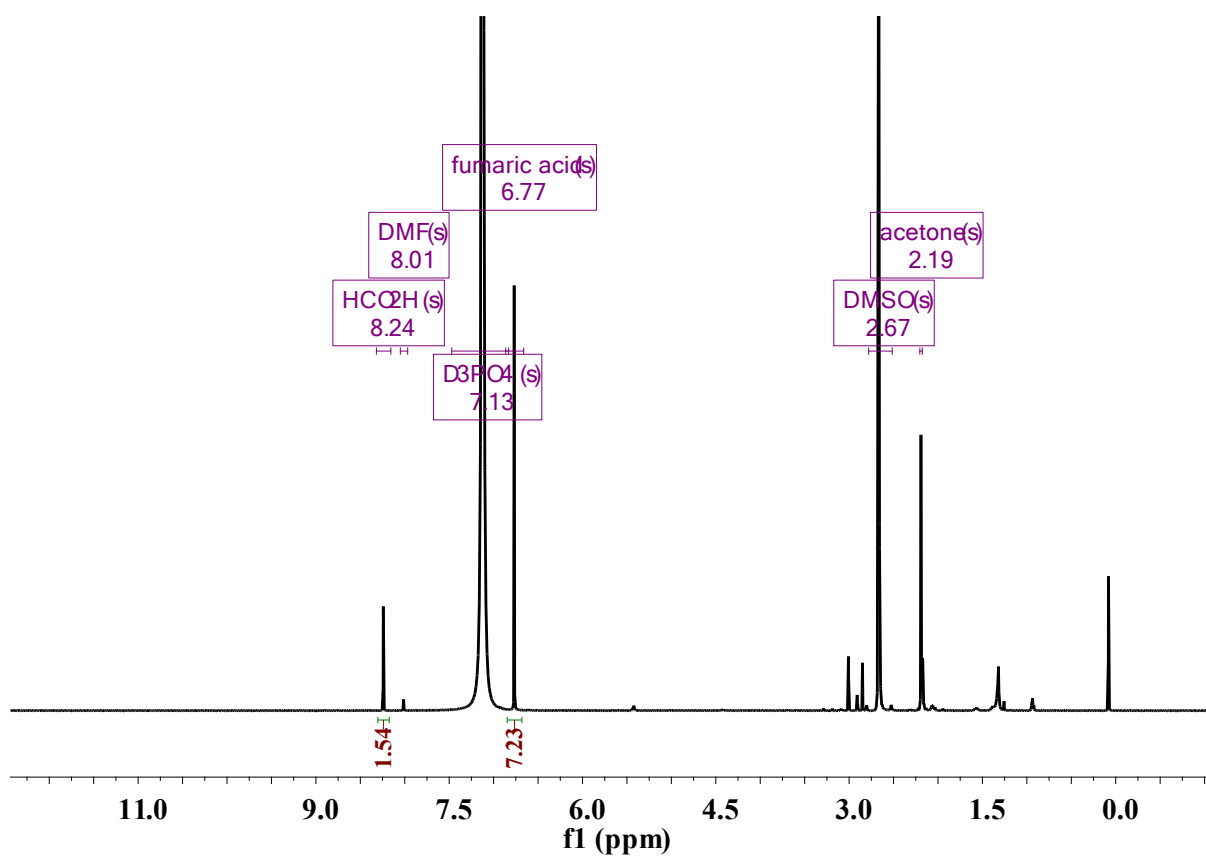


Figure S14. ^1H NMR spectrum of MOF-801 digested in $\text{D}_3\text{PO}_4/\text{D}_2\text{O}/\text{DMSO-}d_6$.

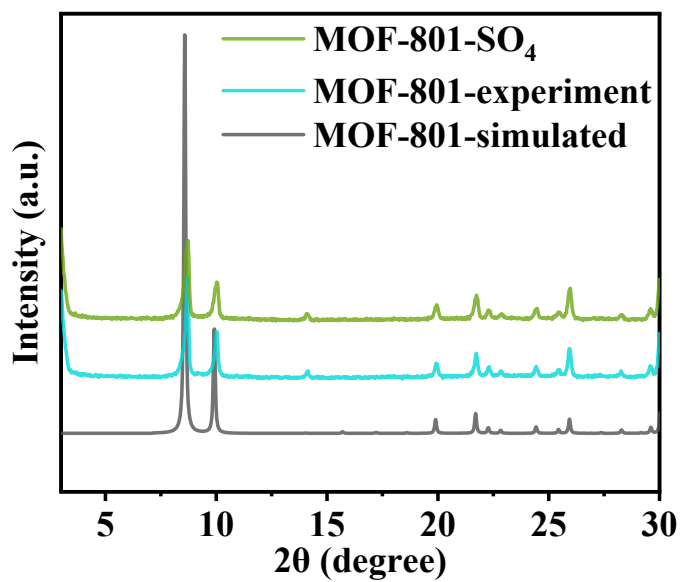


Figure S15. PXRD patterns of MOF-801 and MOF-801- SO_4 .

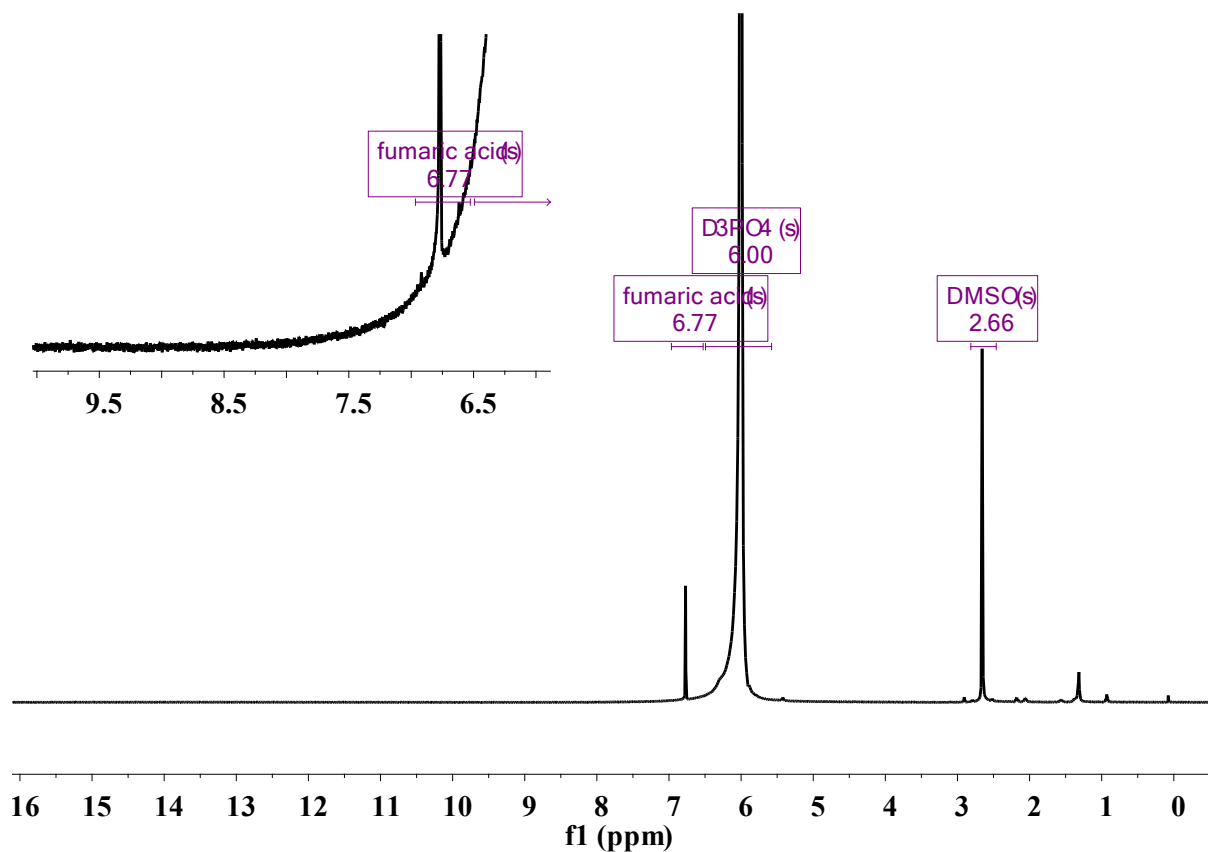


Figure S16. ^1H NMR spectrum of MOF-801- SO_4 digested in $\text{D}_3\text{PO}_4/\text{D}_2\text{O}/\text{DMSO-}d_6$. After dealing with sulfate acid solution, there was no formate observed in ^1H NMR spectrum after digested.

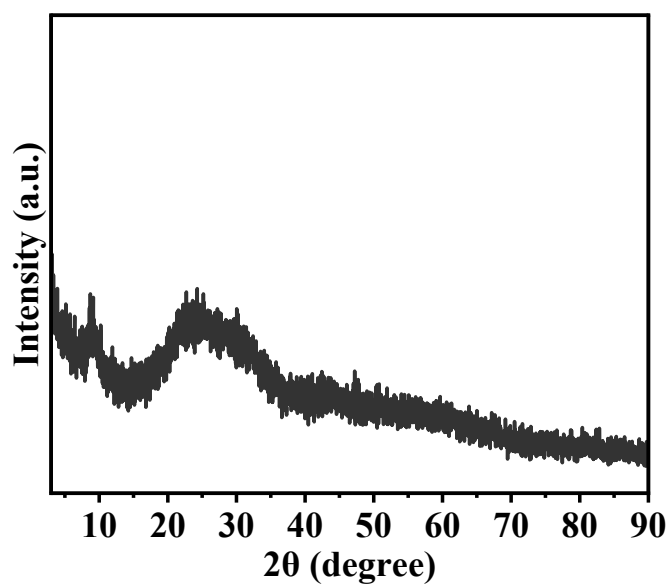


Figure S17. PXRD pattern of MOF-801- SO_4 -Pd.

Synthesis and Characterization of MOF-808-Pd.

Synthesis of MOF-808-OH: 100 mg MOF-808 was immersed in 1 M HCl solution 50 mL, sealed and then put in 80 °C oven for one day. When the temperature dropped to room temperature, the white powder was centrifuged and washed with water for three times, then the obtained MOF-808-OH was dried in a 60 °C vacuum oven overnight.

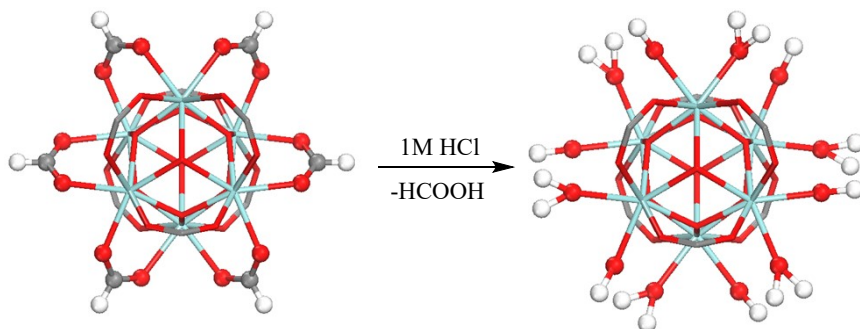


Figure S18. Preparation and structure of MOF-808-OH.

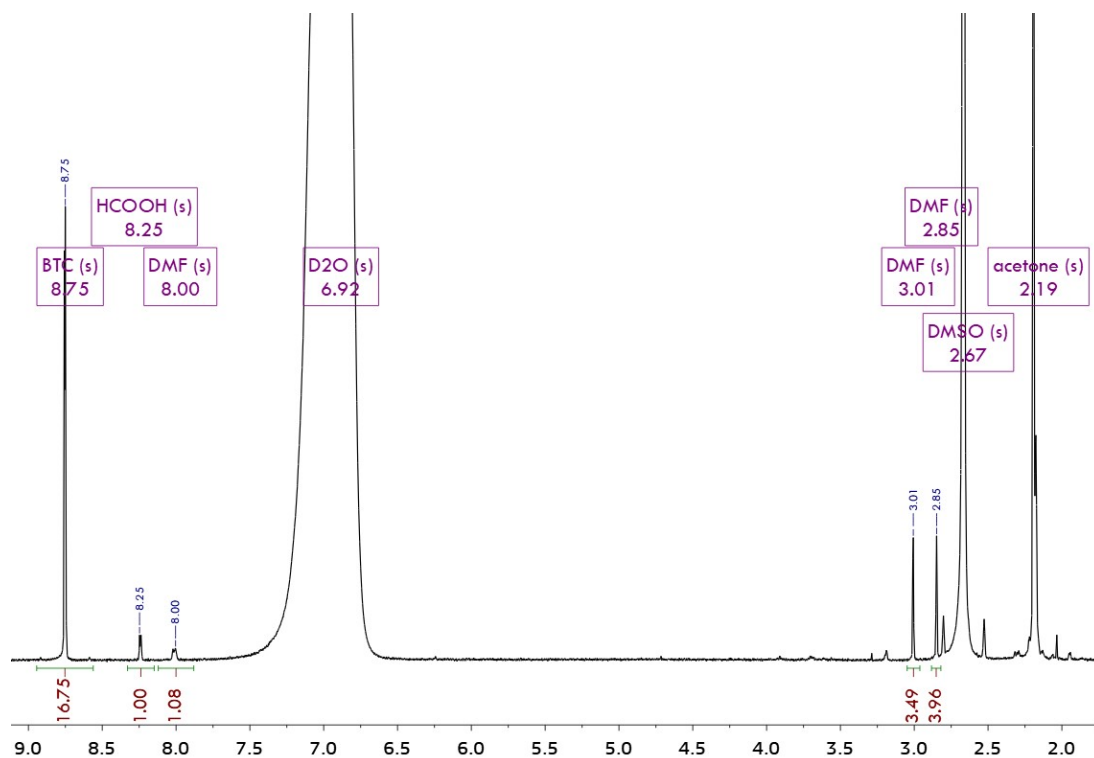


Figure S19. ^1H NMR spectrum of MOF-808-OH digested in $\text{D}_3\text{PO}_4/\text{D}_2\text{O}/\text{DMSO-}d_6$. There was 0.36 HCO_2H per Zr_6 SBU after dealing with HCl.

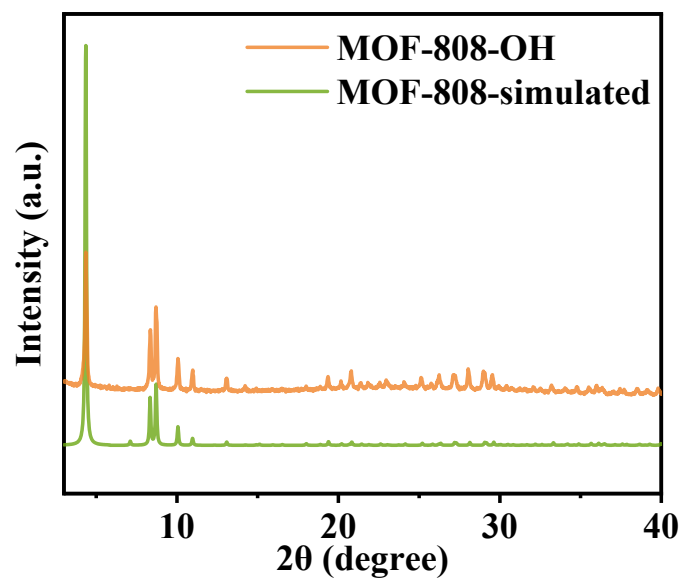


Figure S20. PXRD patterns of MOF-808-OH.

Synthesis of MOF-808-Pd: 50 mg of MOF-808-OH was solvent exchanged with DCM for two days. Then, the sample was immersed in 12 mL of 15 mM Pd(OAc)₂ solution of DCM for 1 day, and then washed by fresh DCM three times followed by vacuum dried. Yellow brown colored powder was obtained.

15 mg NaBH₄ was dissolved in 30 mL H₂O, 50 mg of MOF-808-Pd(OAc)₂ was then dispersed and stirred for 1 hour. The obtained solution was centrifuged out and washed with ultrapure water for three times, then MOF-808-Pd was obtained after vacuum dried.

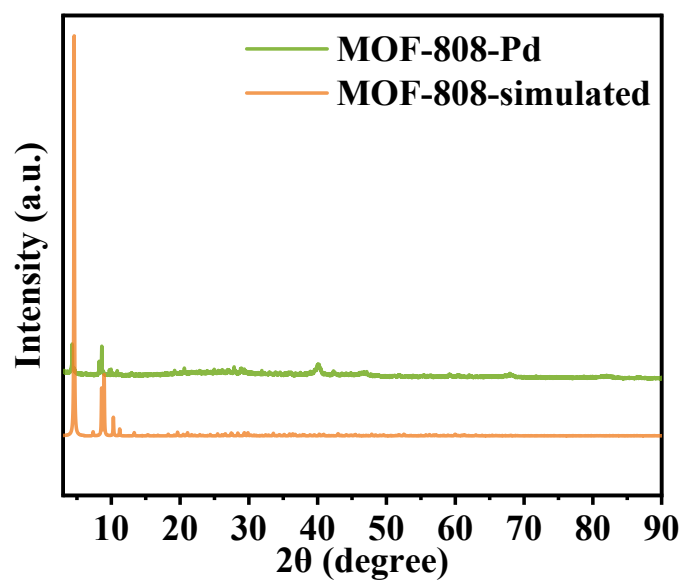


Figure S21. PXRD patterns of MOF-808-Pd.

Table 1. The content of loading metal in varies of catalysts.

| Catalyst | M Content (%) | The number of M per Zr ₆ cluster |
|-----------------------------|---------------|---|
| MOF-808-SO ₄ -Pd | 13.5 | 2.5 |
| MOF-801-SO ₄ -Pd | 7.3 | 1.2 |
| MOF-808-Pd | 9.2 | 1.3 |
| MOF-808-SO ₄ -Pt | 5.8 | 1.1 |
| MOF-808-SO ₄ -Cu | 10.3 | 2.5 |
| MOF-808-SO ₄ -Ni | 10.2 | 2.7 |

Table 2. The SO₄ content in varies of catalysts.

| Catalyst | The number of SO ₄ per Zr ₆ cluster |
|-----------------------------|---|
| MOF-808-SO ₄ -Pd | 2.5 |
| MOF-808-SO ₄ -Pt | 2.5 |
| MOF-808-SO ₄ -Cu | 2.5 |
| MOF-808-SO ₄ -Ni | 2.5 |
| MOF-801-SO ₄ -Pd | 1.2 |

Section S3. Characterization of Catalysts After Reaction.

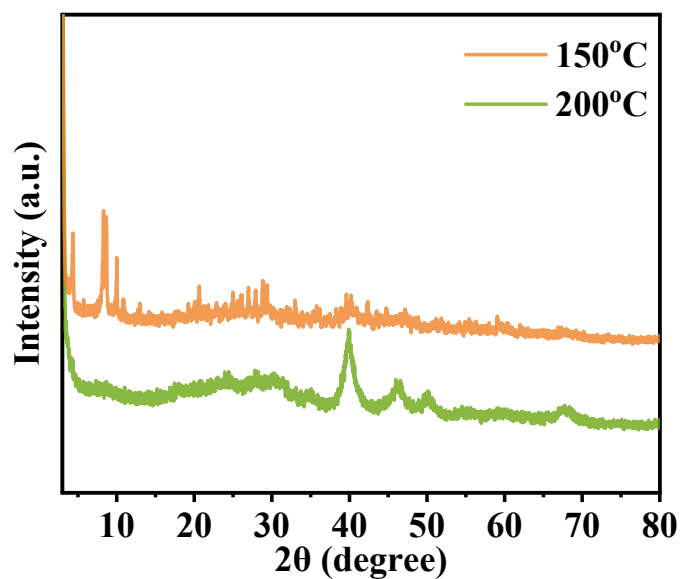


Figure S22. PXRD patterns of MOF-808-SO₄-Pt after a 20-h run of glycerol hydrogenation at different temperature.

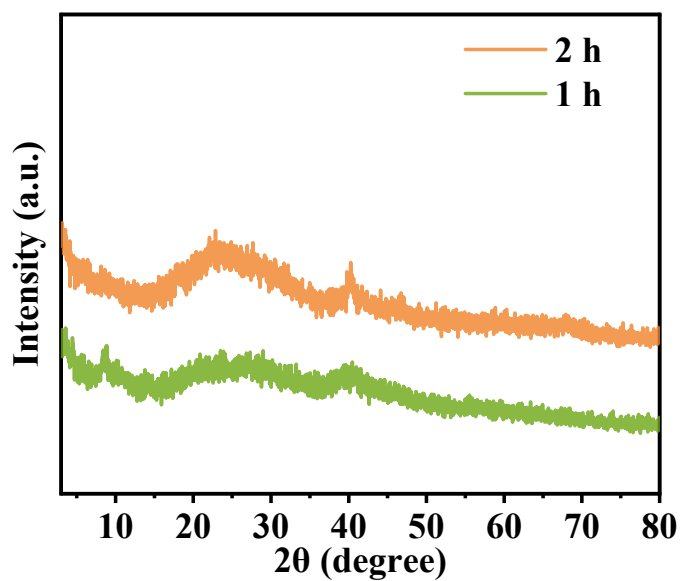


Figure S23. PXRD patterns of MOF-808-SO₄-Pd after 1 h and 2 h glycerol hydrogenation at 200 °C.

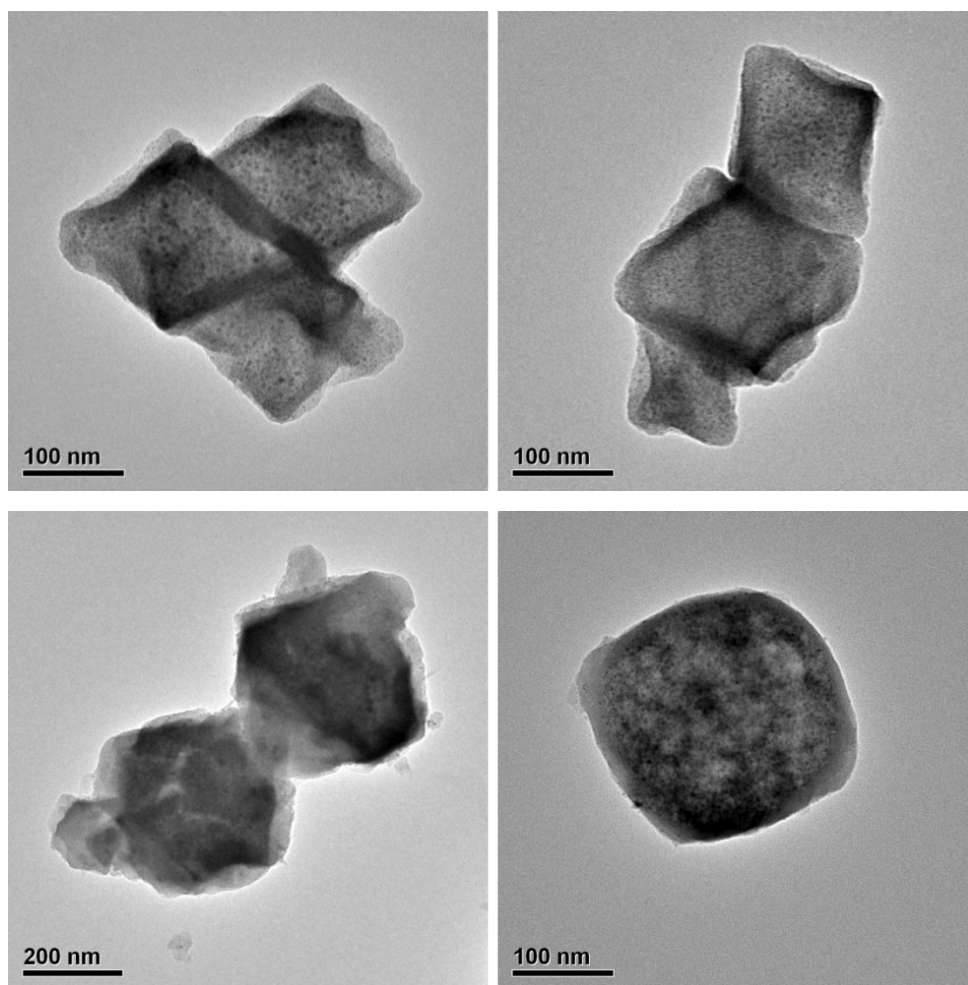


Figure S24. TEM images of MOF-808-SO₄-Pd after 1 h (ontop) and 2 h (below) glycerol hydrogenation at 200 °C.

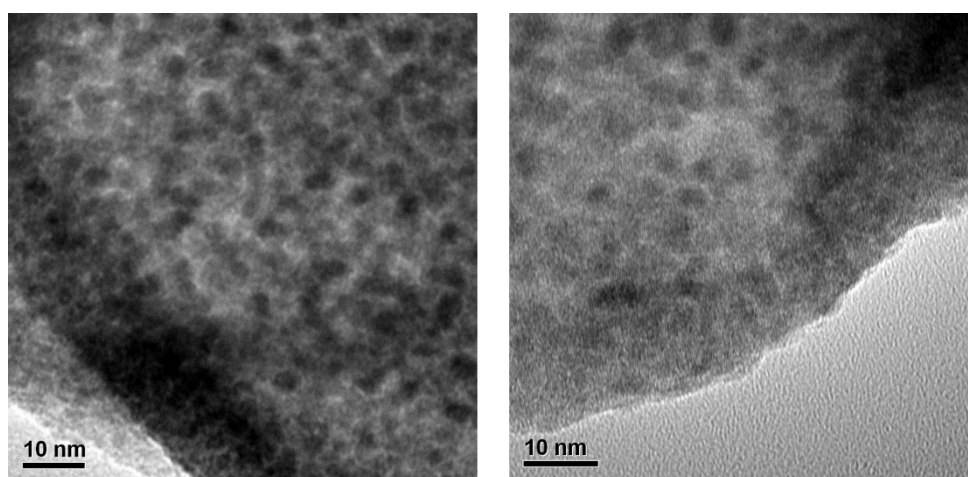


Figure S25. High resolution TEM images of MOF-808-SO₄-Pd after glycerol hydrogenolysis reaction at 150 °C.

References

- (1) Li, T.; Fu, C.; Qi, J.; Pan, J.; Chen, S.; Lin, J. Effect of zinc incorporation manner on a Cu-ZnO/Al₂O₃ glycerol hydrogenation catalyst. *Reaction Kinetics Mechanisms and Catalysis* **2013**, 109 (1), 117-131.
- (2) Valekar, A. H.; Cho, K.-H.; Chitale, S. K.; Hong, D.-Y.; Cha, G.-Y.; Lee, U. H.; Hwang, D. W.; Serre, C.; Chang, J.-S.; Hwang, Y. K. Catalytic transfer hydrogenation of ethyl levulinate to γ -valerolactone over zirconium-based metal-organic frameworks. *Green Chem.* **2016**, 18 (16), 4542-4552.