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Electronic Supplementary Information for

MOFs and their grafted analogues: regioselective epoxide ring-opening with Zr_6 nodes

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Materials Synthesis

Zr_6 cluster. 2.1 mL (5.0 mmol) of $Zr(OPr)_4$ (70% solution in *n*-propanol, Sigma Aldrich, as received) was mixed under an Ar atmosphere with a solution of 16.0 g (131 mmol) benzoic acid in 50 mL of dried, degasified *n*-propanol. The suspension was refluxed for 2 h, after which a white precipitate appeared. Upon filtration, 1.3 g solid (yield: 58%) was separated and subsequently dried under dynamic vacuum (<50 mTorr) for 24 h. The crystal structure was confirmed via PXRD (Figure S1).

NU-1000. Synthesis of NU-1000 followed a literature procedure previously reported by some of us.[1] Activation of the material, also following protocol, is as follows: approximately 50 mg of the catalyst was soaked in a mixture of 12 mL DMF and 0.5 mL 8 M $HCl_{(aq)}$ in a sealed vessel. The vessel was heated at 100C for 18 h, after which the solids were washed with DMF (3 × 10 mL) and acetone (3 × 10 mL) before drying under dynamic vacuum (<50 mTorr) for 24 h before catalytic use. The crystal structure was confirmed using PXRD (Figure S2).

MOF-808. MOF-808 synthesis followed a previously reported literature protocol.[2] Activation of MOF-808, also following protocol, was achieved by drying on a supercritical CO2 dryer, followed by dehydration under dynamic vacuum (<50 mTorr) at 150°C for 24 h. The resulting crystal was confirmed using PXRD (Figure S3).

Zr_6-P-SiO_2. 0.11 mmol Zr_6 cluster were evacuated and purged with N_2 on a Schlenk line, then dissolved in 50 mL anhydrous, degasified toluene and stirred at RT for 10 min. Then, 1.0 g ethylphophonic acid silica (“P-SiO_2,” Sigma Aldrich, 45-86 µm, 524 m^2 g^{-1}, 4.9 nm avg. pore dia.), previously dehydrated at 110°C for 10 h under dynamic vacuum, was added to the mixture. The suspension was refluxed for 14 h, vacuum-filtered in air, washed with toluene (3 × 15 mL) and diethyl ether (3 × 20 mL) and dried under dynamic vacuum (<50 mTorr) for 24 h.

Zr_6-BA-SiO_2. Benzoic acid-modified silica support ("BA-SiO_2," 561 m^2 g^{-1}, 0.42 mmol BA g^{-1} (TGA)) was synthesized and characterized as part of a prior investigation reported by some of us for alkene epoxidation systems.[3, 4] 0.15 mmol Zr_6 cluster were loaded into a flask under N_2 purge and dissolved in 25 mL anhydrous, degasified toluene at RT. After stirring for 15 min, 0.5 g BA-SiO_2 (dehydrated at 110°C for 10 h under dynamic vacuum) was added to the solution, and the suspension was refluxed for 14 h. After the suspension cooled, solids were vacuum-filtered in air, washed with anhydrous toluene (3 × 10 mL) and diethyl ether (3 × 15 mL) and subsequently dried under dynamic vacuum (<50 mTorr) at RT for 24 h.

Zr_6-SiO_2. 0.072 mmol Zr_6 was dissolved in 1.9 mL toluene, and the solution was added dropwise while stirring to a beaker containing 2.0 g SiO_2 (Selecto, 32-63 µm, 569 m^2 g^{-1}, 5.4 nm avg. pore dia., 0.95 cm^3 g^{-1} pore vol.). The SiO_2 was partially dehydroxylated at 300°C for 10 h under dynamic vacuum (<50 mTorr) prior to use. The impregnated material was dried at RT for 24 h to remove the solvent, then calcined in air at 550°C for 6 h at a ramp rate of 10°C min^{-1}.

Zr-SiO_2. Zr-SiO_2 from grafted dimethoxycalix[4]arene-Zr-Cl_2[5] was synthesized and characterized as part of a previous investigation reported by some of the authors for alkene epoxidation systems.[6] Like Zr_6-SiO_2, this material was also calcined at 550°C for 6 h at a ramp rate of 10°C min^{-1} immediately before catalytic use.

Experimental Methods and Instrumentation

Spectroscopy. Diffuse reflectance UV-visible spectroscopy (DR UV-vis) was collected from 800 to 200 nm at ambient conditions using a Shimadzu UV-3600 Spectrophotometer equipped with a Harrick Praying Mantis diffuse reflectance accessory. Polytetrafluoroethylene powder (Sigma Aldrich) was used as a perfectly reflecting material to collect a baseline for Kubelka-Munk pseudoabsorbance ($F(R)$) and further as a 20:1 diluent for catalyst materials. Optical edge energies were determined from calculating the x-intercept of an indirect Tauc plot ($[F(R)\cdot hv]^{1/2}$ vs. hv, where hv energy is in units of eV).[7, 8] Solid-state ^{31}P cross polarization magic angle spinning (CP-MAS) NMR spectra were obtained on a 400 MHz Varian spectrometer at a spin rate of 5 kHz. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was collected on a Nicolet 7600 FT-IR spectrometer equipped with a MCT detector from 4000 to 650 cm^{-1} wavenumbers at 120°C under flowing He using KBr as a reference material.

Surface loadings. Zr and P loadings were quantified using inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Thermo iCAP 7600 instrument calibrated against serial dilution of commercial standards (Fluka Analytical) in 0.9 wt% $HNO_{3(aq)}$. Catalysts were digested in concentrated hydrofluoric acid (48 wt% in H_2O, Macron) and diluted with 0.9 wt% $HNO_{3(aq)}$ prior to analysis. [CAUTION: Handle and store concentrated HF with extreme care.] Multiple trials were averaged. Separately, organic content of BA-SiO_2 was determined using thermogravimetric analysis on a TA Instruments Q500 under dry synthetic air (90% O_2, 10% N_2, 100 mL min^{-1}), from RT to 800°C at a ramp rate of 10°C min^{-1}. Metal and organic content were normalized to BET surface area of the SiO_2 support prior to Zr precursor deposition, as determined by the Brunauer-Emmett-Teller analysis method for N_2 physisorption at 77 K using a

Micromeritics ASAP 2010 instrument. The BET surface area of NU-1000 and MOF-808 were obtained via N_2 physisorption at 77 K using a Micromeritics Tristar II 3020 instrument.

X-ray diffraction. Powder X-ray diffraction (PXRD) spectra were collected on a Rigaku ATXG Diffractometer with Cu K_α rotating anode radiation source. Spectra were collected from 2°-30° with a step width of 0.05°. Experimental diffraction patterns were verified with simulated spectra using simulation features of the MDI Jade 2010 analysis software. See Figures S1-S3 and S8.

Potentiometric titrations. Potentiometric titrations were performed using a Metrohm Titrando 905 autotitrator, equipped with a Dosino 800 dosing units (20 mL and 10 mL), calibrated using commercial pH buffer solutions (Metrohm; pH = 2.00, 4.00, 7.00, 9.00) using a procedure previously reported by some of us.[9] In brief, catalyst samples (30 mg) were ground with a mortar and pestle before being dispersed in 36 mL of a 0.01 M aq. $NaNO_3$ solution. After equilibration for 18 h, the solution pH was adjusted to 3.0 using 0.1 M aq. HCl. The suspensions were titrated with 0.1 M aq. NaOH to a final pH of 10.5-11, with 0.025 mL injection volumes at a rate of 0.020 mL min^{-1}. Equivalence points were determined using first derivative plots of d(pH)/dV vs. V, where V is the volume of titrant added (mL). Resulting pK_a values were computed as the pH value at one-half the titrant volume added to achieve the equivalence point. See Figure S6 and Table S1. For the P-SiO_2 support, two d(pH)/dV derivative peaks were observed (Figure S6(e)), and the data was subjected to Lorentzian function curve-fitting using WaveMetrics IGOR Pro 6.36 software.

Product standards. Primary and secondary alcohol products for the ring-opening of 1,2-epoxyoctane with isopropanol are not commercially available and were synthesized and purified for GC calibration. 5.0 mmol of 1,2-epoxyoctane (97%, Alfa Aesar, as received) were added to a mixture of 20 mmol isopropanol and 0.0050 mmol tris(pentafluorophenyl)borane (95%, Acros Organics, as received), and the solution was reacted at 60°C for 24 h. Three separate batches were combined, and products were purified by flash chromatography using 9:2 *n*-hexane/ethyl acetate over mesoporous SiO_2 (SorbTech, 40-63 µm, 6.0 nm avg. pore dia.). Purified products were identified using a Shimadzu QP2010 GC-MS and calibrated to standards of known concentration with mesitylene (internal standard) using an Agilent HP 6890 GC-FID. Each GC was equipped with a Zebron ZB-624 capillary column (30 m × 0.25 mm × 1.4 µm).

Catalysis. In a typical reaction, 6.9 mmol 1,2-epoxyoctane was measured into a 20 mL screw-top, septum-cap vial that contained 0.069 mmol Zr catalyst (1.0 mol% Zr), 28 mmol isopropanol and 7.0 mmol mesitylene (internal standard and diluent). The reaction vial was sealed, shaken at 700 rpm and heated to 55°C in a Glas-Col heated vortexer to begin the reaction. Aliquots (50 µL) were withdrawn at specified time intervals until 24 h, collected using a syringe equipped with a Whatman glass microfiber filter to remove suspended catalyst particles. Aliquots were diluted with 1.5 mL THF and analyzed via GC-FID. Product concentrations were calibrated against known concentrations of purified primary and secondary alcohol products. After 24 h, some reaction mixtures were vacuum-filtered (while hot), and the filtered solids were washed with acetone. Recovered solids were dried at RT in air overnight, followed by drying under dynamic vacuum (<50 mTorr) before subsequent analysis via PXRD (NU-1000 and MOF-808; see Figure S8) or ICP-OES (Zr_6-P-SiO_2, Zr_6-BA-SiO_2, Zr_6-SiO_2, Zr-SiO_2; see Table S2).

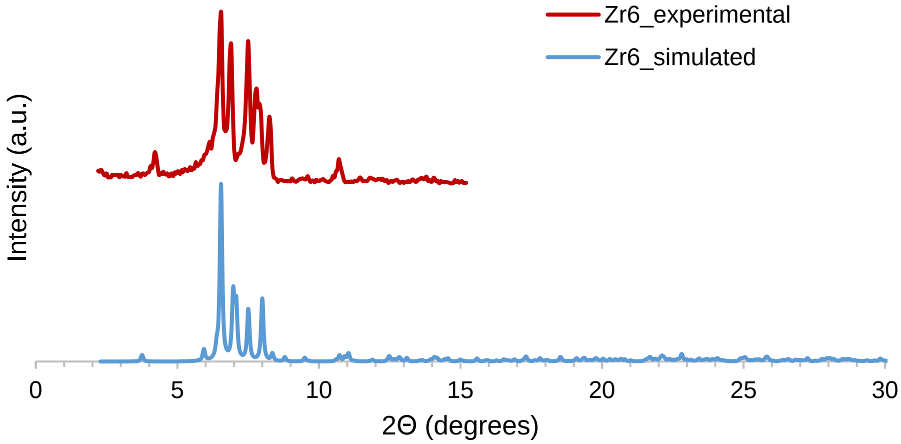


Figure S1. Experimental and simulated PXRD of Zr_6-benzoate cluster.

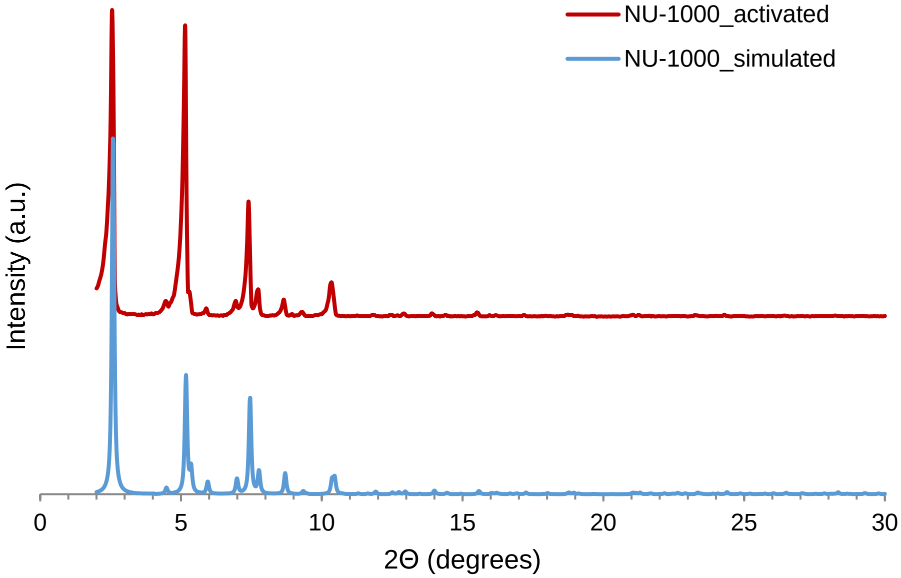


Figure S2. Experimental and simulated PXRD of NU-1000.

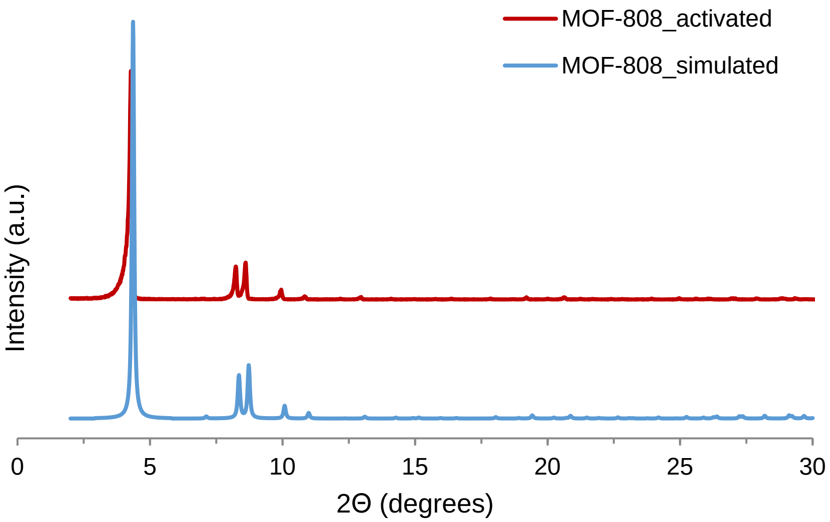


Figure S3. Experimental and simulated PXRD of NU-1000.

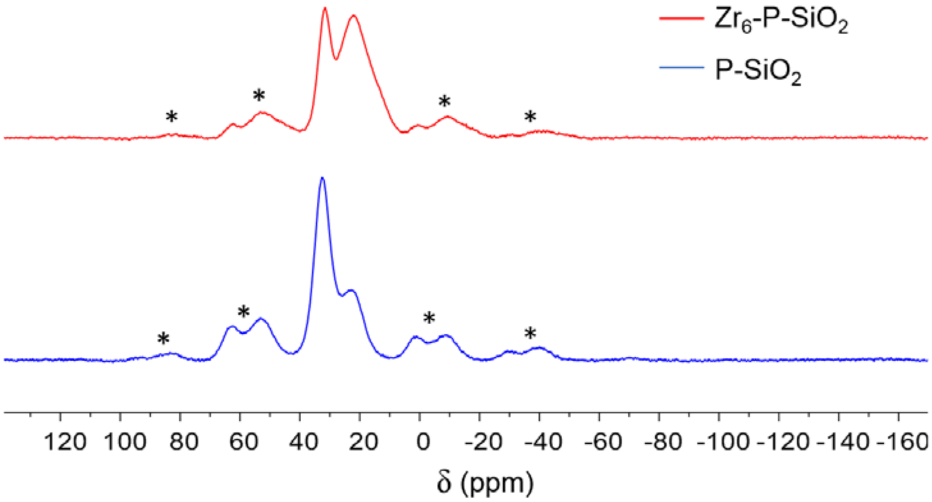


Figure S4. ^{31}P CP-MAS NMR of Zr_6-P-SiO_2 (as-synthesized) and P-SiO_2 (as-received) collected at a spin rate of 5 kHz. The feature at 32 ppm is a di-acid phosphorus, while the feature at 22 ppm corresponds to a coordinated phosphorus.[10] For P-SiO_2, this is likely due to uncleaved ethoxy groups (from material preparation), whereas for Zr_6-P-SiO_2 it is attributed to an immobilized Zr_6 cluster. The substantial increase in this feature for Zr_6-P-SiO_2 indicates coordination to the P-SiO_2 surface. Asterisks denote spinning sidebands.

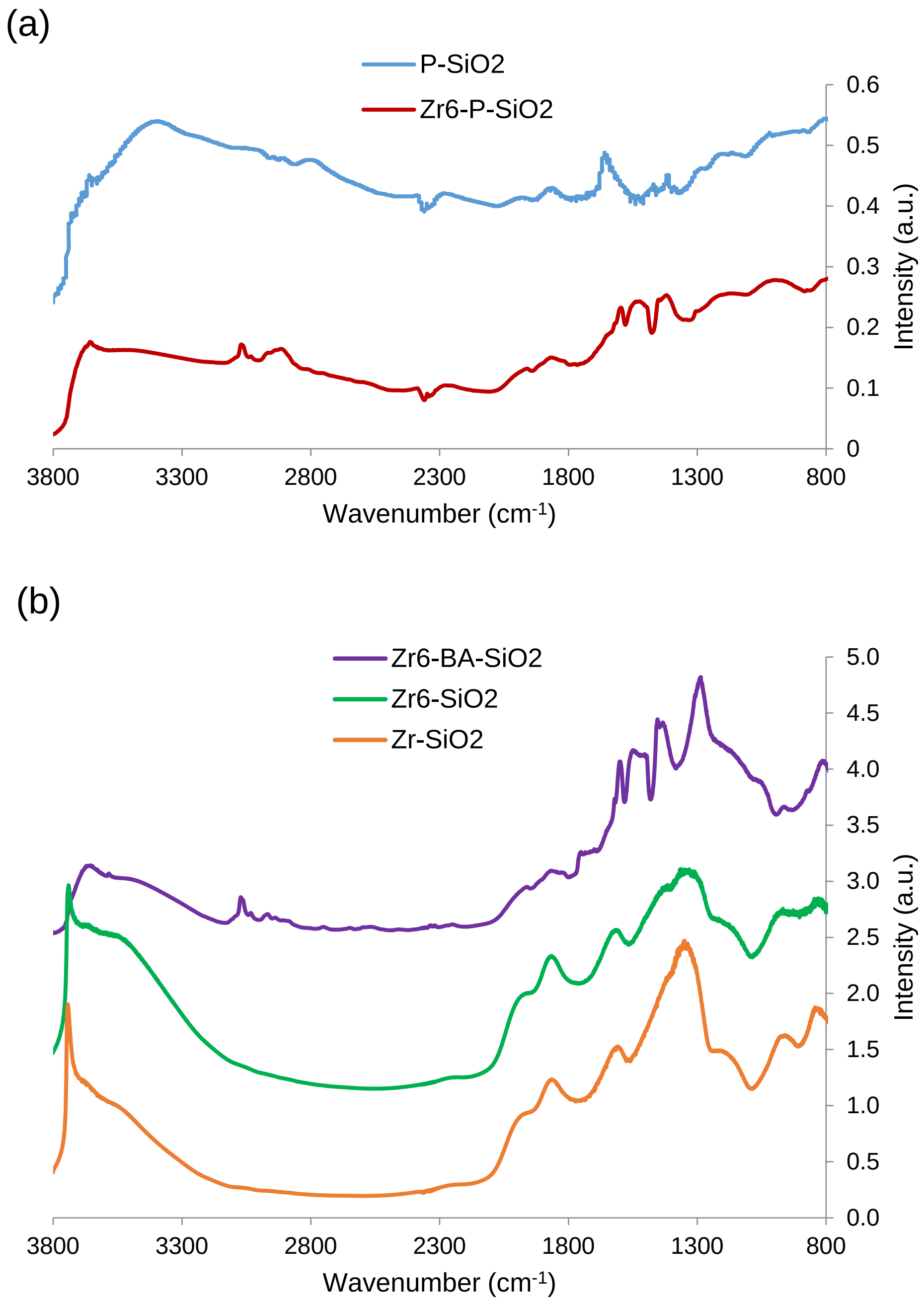


Figure S5. DRIFTS of (a) P-SiO_2 (blue; as-received) and Zr_6-P-SiO_2 (red; as-synthesized), and of (b) Zr_6-BA-SiO_2 (purple; as-synthesized), Zr_6-SiO_2 (green; calcined), and Zr-SiO_2 (orange, calcined). All spectra collected at 120°C under flowing He.

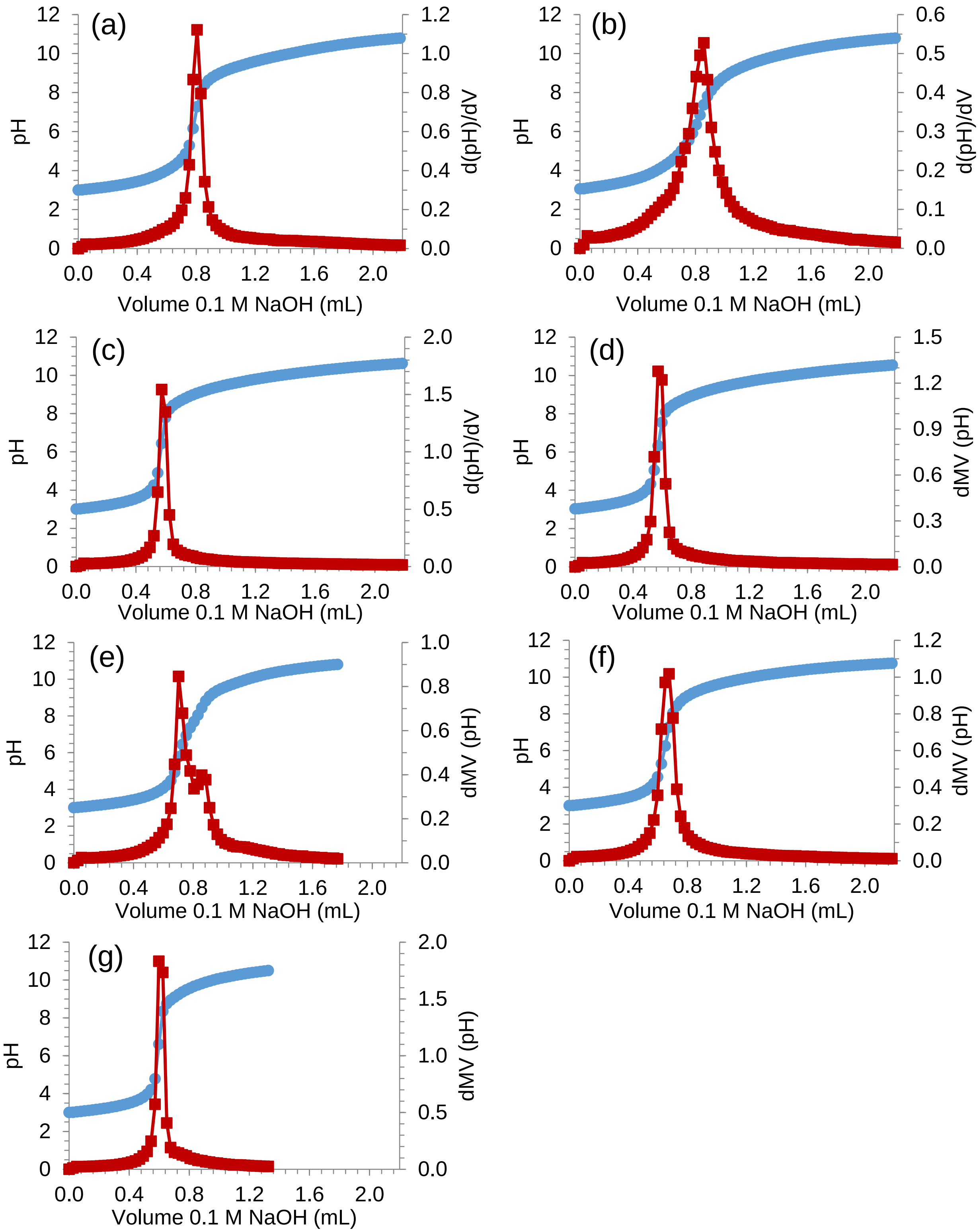


Figure S6. Potentiometric acid-base titration curves (pH, blue; left-hand *y*-axis) and first derivative curves (d(pH)/dV, red; right-hand *y*-axis) vs. volume (V) of 0.1 M NaOH titrant added (mL) of various materials: (a) Zr_6-P-SiO_2, (b) Zr_6-BA-SiO_2, (c) Zr_6-SiO_2, (d) Zr-SiO_2, (e) P-SiO_2, (f) BA-SiO_2, and (g) unmodified SiO_2.

Table S1. Potentiometric titration data for supported materials. See Figure S6, Experimental Methods and reference 9.

Material	**Total Acid Site Density (mmol g^{-1})**	**pK_a**
Zr_6-P-SiO_2	2.7	3.5
Zr_6-BA-SiO_2	2.8	3.6
Zr_6-SiO_2	1.9	3.3
Zr-SiO_2	1.9	3.3
P-SiO_2	2.8	3.4; 7.3*
BA-SiO_2	2.4	3.3
unmodified SiO_2	2.0	3.3

* From second feature in first derivative plot. See Experimental Methods and Figure S6(e).

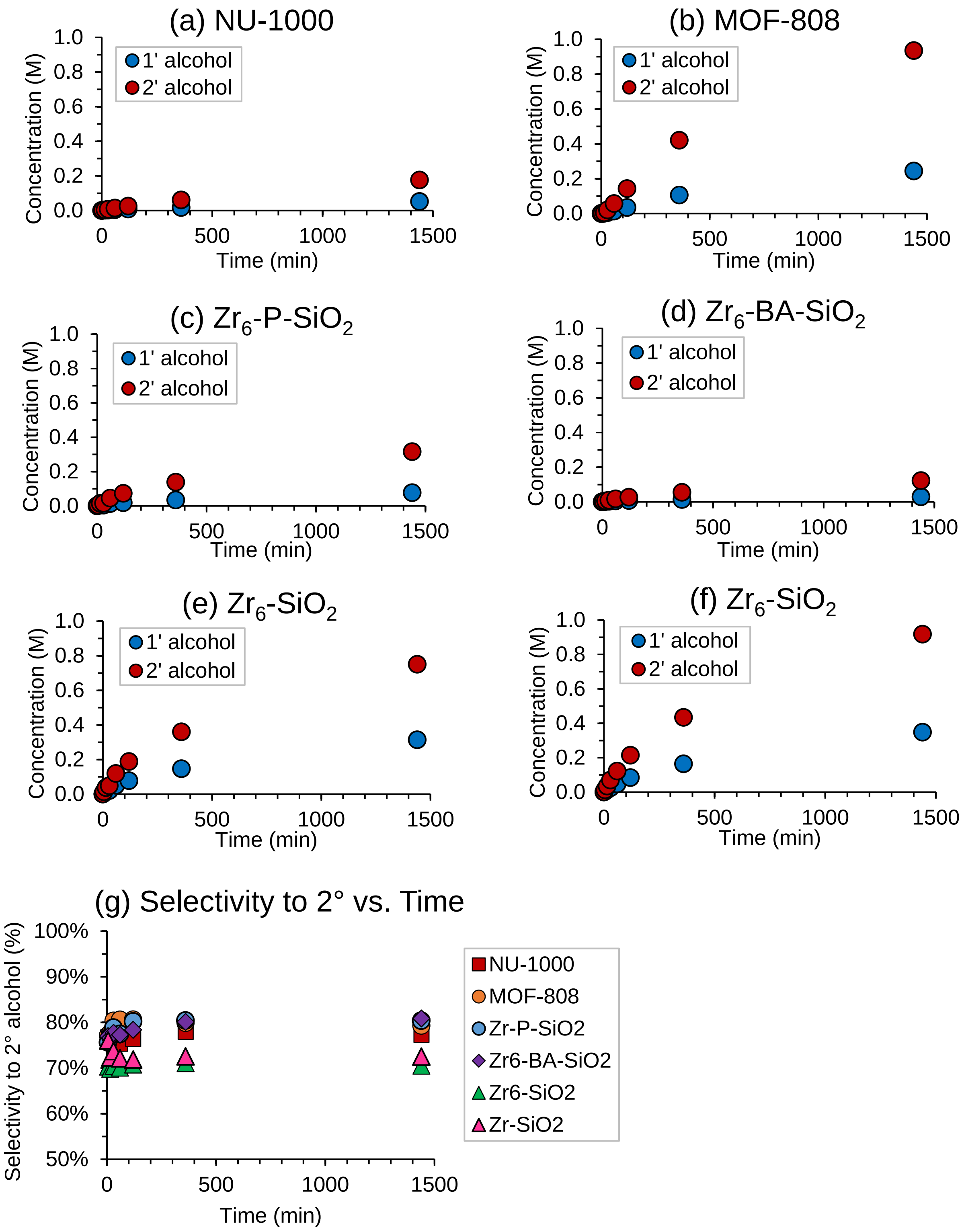
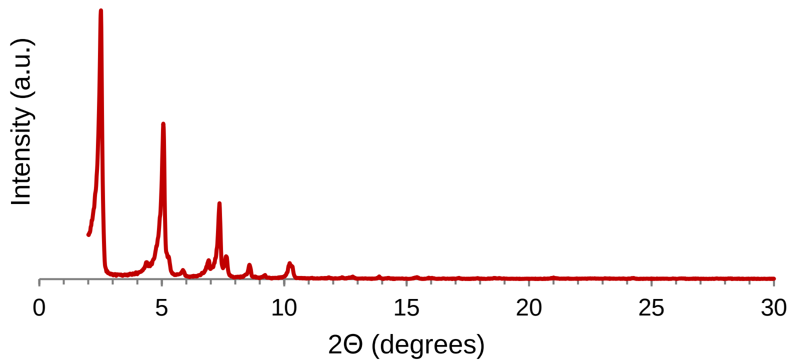


Figure S7. Product concentration timecourse data of catalysts (a) NU-1000, (b) MOF-808, (c) Zr_6-P-SiO_2, (d) Zr_6-BA-SiO_2, (e) Zr_6-SiO_2, and (f) Zr-SiO_2; and (g) integrated selectivity to 2° alcohol product vs. time. See main text and Experimental Methods for standard reaction conditions.

(a) NU-1000, spent/washed



(b) MOF-808, spent/washed

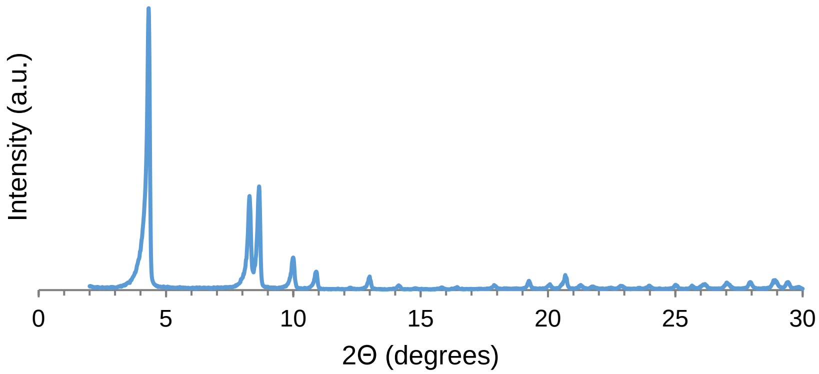


Figure S8. PXRD patterns of spent and acetone-washed MOF catalysts (a) NU-1000 and (b) MOF-808. See Experimental Methods.

Table S2. Zr elemental analysis of fresh and spent/acetone-washed supported catalysts Zr_6-P-SiO_2, Zr_6-BA-SiO_2, Zr_6-SiO_2 and Zr-SiO_2. See Experimental Methods.

Catalyst	**Zr content (mmol g^{-1})**	
	Fresh	**Spent/Washed**
Zr_6-P-SiO_2	0.54	0.55
Zr_6-BA-SiO_2	0.78	0.79
Zr_6-SiO_2	0.22	0.23
Zr-SiO_2	0.21	0.22

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