Supporting Information

$H_5PV_2Mo_{10}O_{40}$ Polyoxometalate Encapsulated in NU-1000 Metal–Organic Framework for Aerobic Oxidation of a Mustard Gas Simulant

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Section S1. Physical Methods

The supercritical drying process used a TousimisTM Samdri PVT-3D critical point drier in which liquid CO_2 was used to exchange ethanol 4 times over 8 h. The material was then heated above 31 °C (P = 73 atm), the critical point of CO_2 before the instrument was evacuated at a rate of 0.1 sccm.[1–3]

All MOF samples were activated by exposure of 20 to 100 mg of material for 12 hours under high vacuum on a Micromeritics Smart VacPrep instrument. N2 adsorption and desorption isotherm measurements were performed on a Micromeritics Tristar II at 77 K. DFT calculated pore size distributions used the slit geometry and the N2 @ 77 on carbon slit pores by NLDFT kernel.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) samples of solids were prepared in a 2-5 mL Biotage microwave vial by dissolving 1-2 mg of sample in 5 drops of H_2SO_4 and slowly adding 2 mL of HNO_3. The vial was cringe-capped and heated to 150 °C for 15 min in a SPX microwave reactor. The resulting orange-yellow solution was made colorless by adding 0.5 mL H_2O_2 (30 wt% in water) and heating in a sand bath for 10 min. To the colorless or pale solution, 10 mL of deionized water was added, and the resulting dilution analyzed with Thermo iCap7600 ICP-OES spectrometer, equipped with a CCD detector and Ar plasma covering 175-785 nm range.

Powder X-ray diffraction (PXRD) patterns were collected on a Stoe STADI-P instrument. Samples were using Kα1 Cu radiation, a step size of 2θ = 0.015° over a 2θ range of 1 to 25°. Variable temperature powder X-ray diffraction (PXRD) patterns were collected on a Stoe STADI-MP instrument equipped with a furnace using Kα1 Mo radiation.

Solution NMR spectra were collected on a 400 MHz Agilent DD MR-400 system at IMSERC (Integrated Molecular Structure Education and Research Center) at Northwestern University. Solid-state NMR spectra were collected on a Bruker 400 MHz NMR system spinning at 10,000 Hz.

Scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) line scans were collected using a Hitachi SU8030 FE-SEM microscope at Northwestern University's EPIC/NUANCE facility. All samples were coated with ~15 nm of OsO_4 immediately prior to imaging.

GC-FID measurements were carried out on an Agilent Technologies 7820A GC system equipped with an Agilent J&W GC HP-5 capillary column (30 m × 320 µm × 0.25 µm film thickness). All samples were filtered and diluted with dichloromethane prior to injection. Starting temperature: 70 °C, Hold: 0.5 min, Ramp: 30 °C/min, Time: 1 min, Ramp: 75 °C/min, End temperature: 250 °C.

Thermogravimetric analyses (TGA) were performed on a Mettler Toldeo STAR^e TGA/DSC 1 under a N_2 flow at a 10 °C/min ramp rate from 25 to 700 °C. For TGA-MS measurements, a Netzsch Simultaneous Thermal Analysis (STA 449F3) instrument coupled to a GC-MS was used.

X-ray photoelectron spectroscopy measurements were carried out on a Thermo Scientific ESCALAB 250 Xi equipped with an electron flood gun and a scanning ion gun. Analysis used the Thermo Scientific Avantage Data System software, and C1s peak (284.8 eV) peak was used as the reference. Oxidation states of Mo and V were assigned by comparison to previously published data.[4,5]

Section S2. Composite Characterization

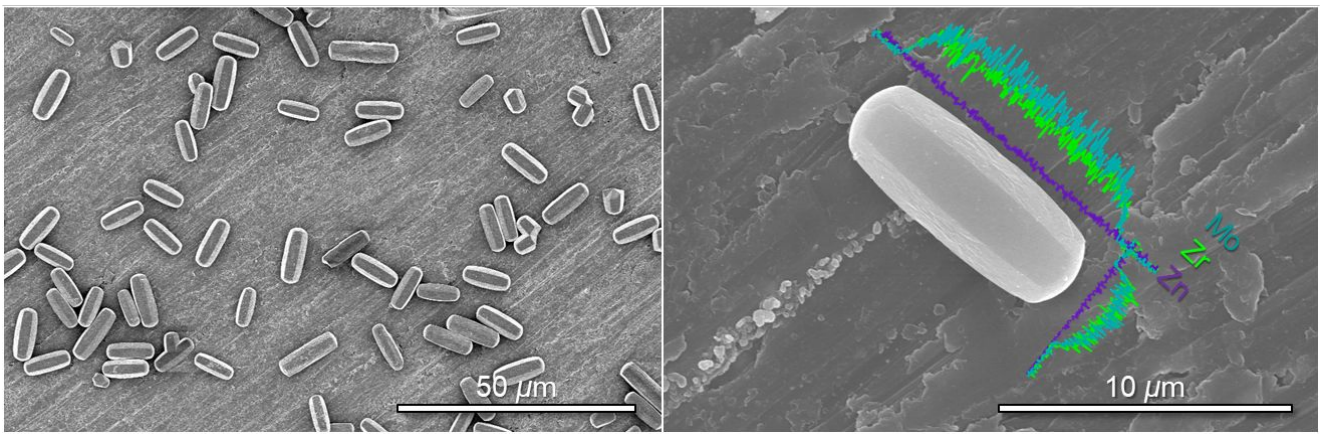

Figure S1. SEM images of NU-1000 before (left) and after (right) $[PV_2Mo_{10}O_{40}]^{5-}$ incorporation. EDS line scans of Mo and Zr compared to baseline Zn.

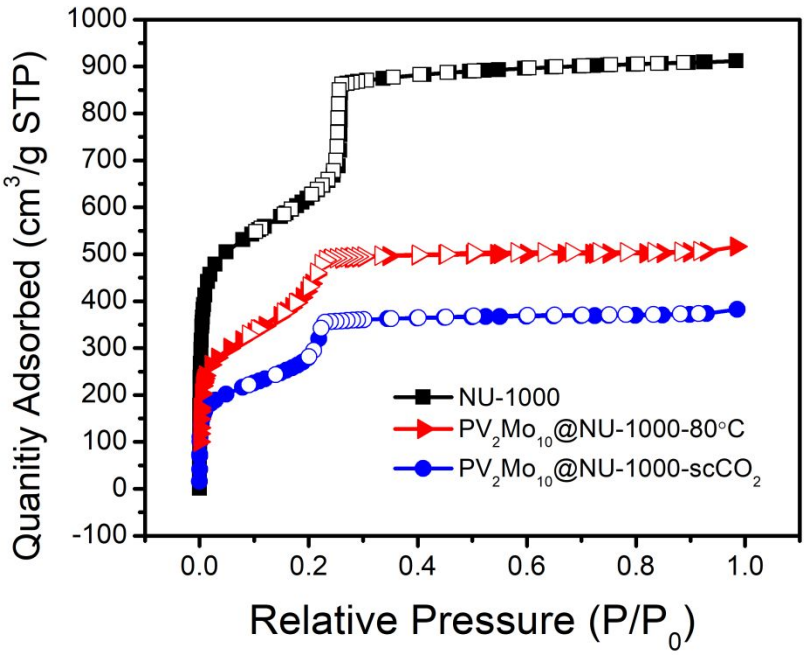

Figure S2. Gravimetric N_2 adsorption (filled) and desorption (unfilled) isotherms for NU-1000 and composites with $[PV_2Mo_{10}O_{40}]^{5-}$.

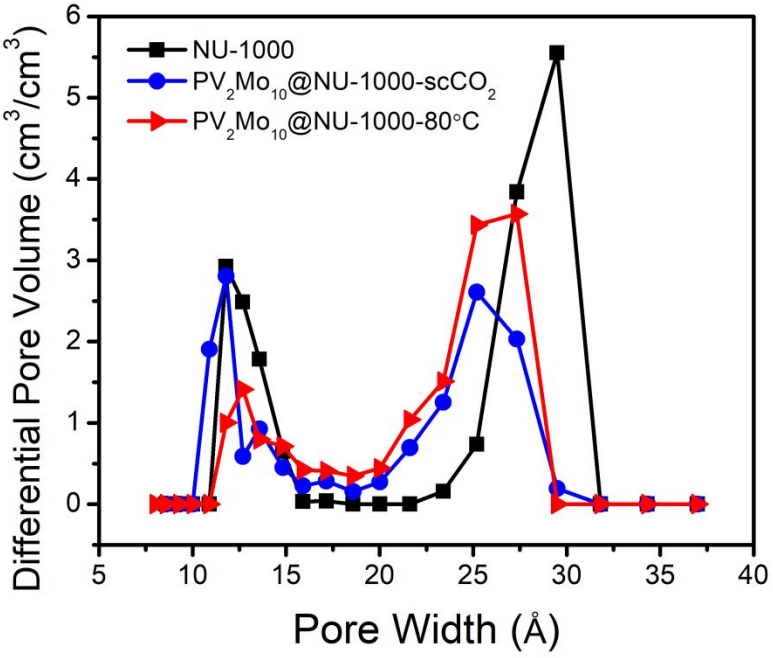

Figure S3. Volumetric DFT-calculated pore size distributions of NU-1000 and PV_2Mo_{10}@NU-1000.

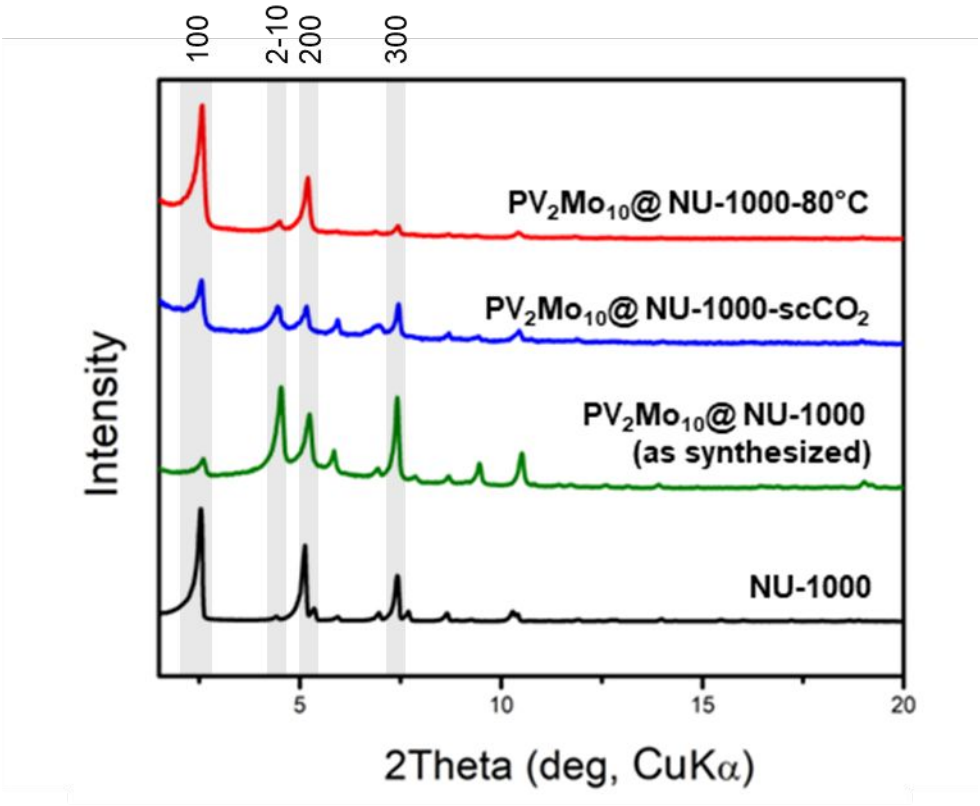

Figure S4. Indexed PXRD patterns of NU-1000, PV_2Mo_{10}@NU-1000-$scCO_2$, and PV_2Mo_{10}@NU-1000-80°C.

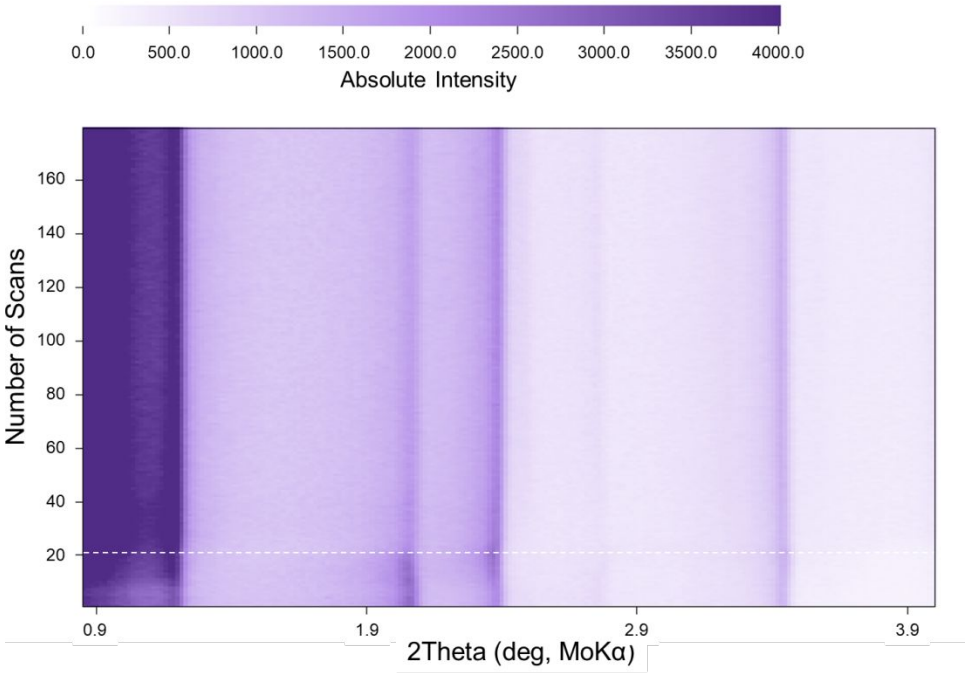

Figure S5. *In situ* variable temperature PXRD patterns for PV_2Mo_{10}@NU-1000-$scCO_2$. N (y-axis) indicates the number of scans taken at 80 °C. Each scan is 1 min apart. The horizontal dotted white line highlights where the structural change occurs.

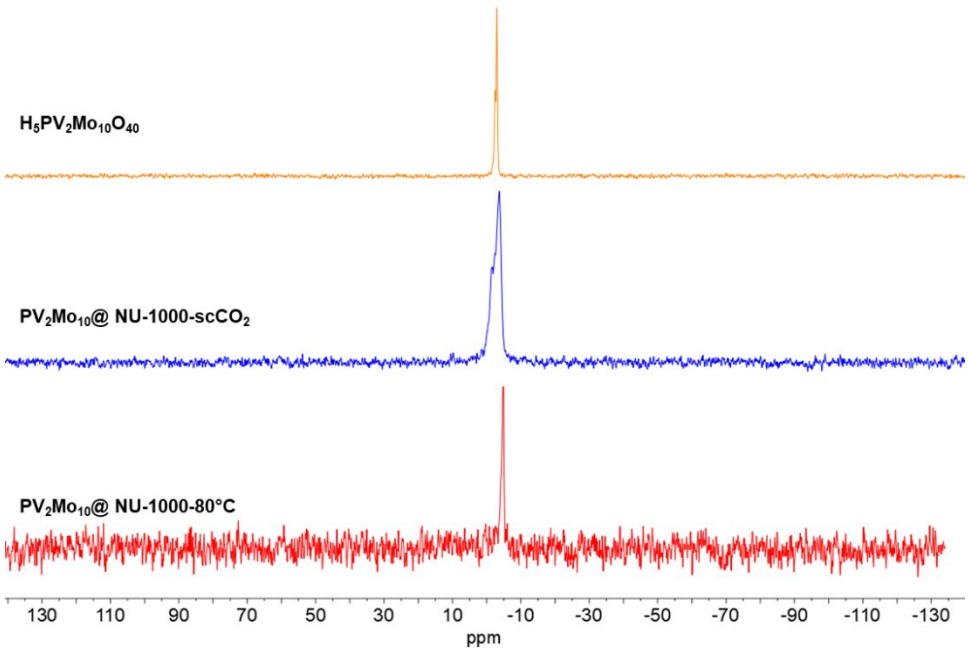

Figure S6. ^{31}P CPMAS NMR spectra of $H_5PV_2Mo_{10}O_{40}$ and PV_2Mo_{10}@NU-1000.

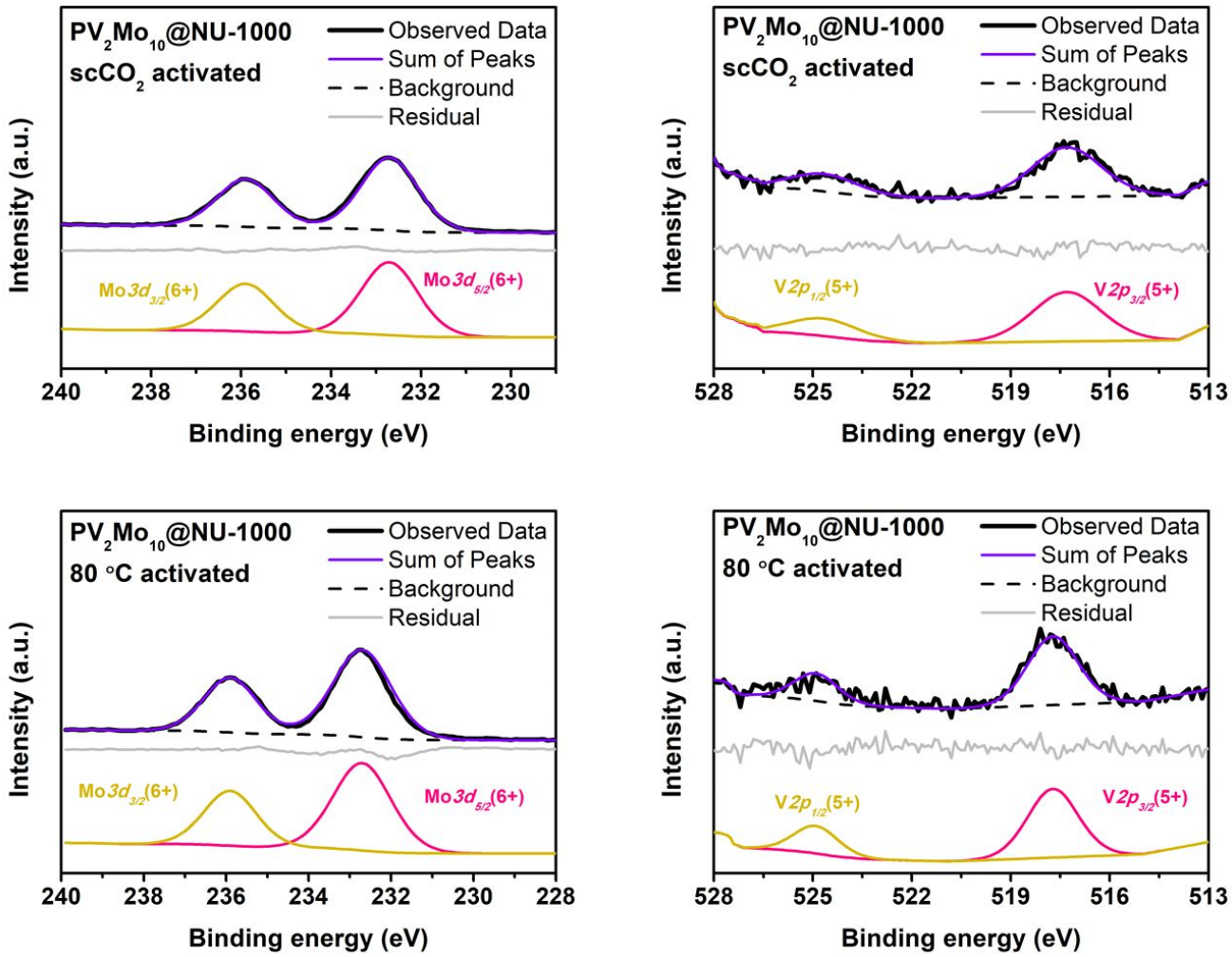

Figure S7. XPS spectra of PV_2Mo_{10}@NU-1000-$scCO_2$ (top) and PV_2Mo_{10}@NU-1000-80°C (bottom) for Mo (left) and V (right).

Section S3. Catalytic Studies

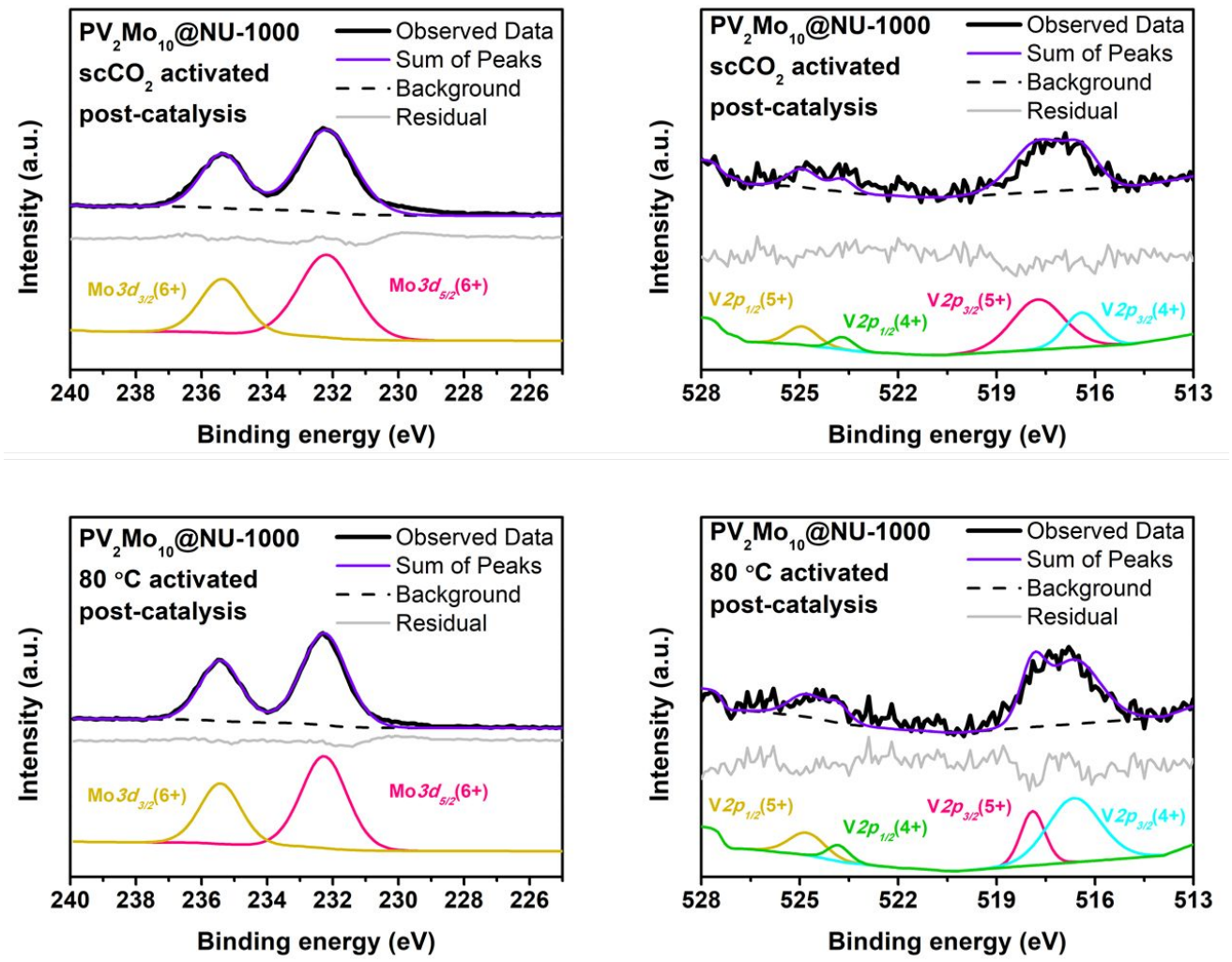

Figure S8. XPS spectra of PV_2Mo_{10}@NU-1000-$scCO_2$ (top) and PV_2Mo_{10}@NU-1000-80°C (bottom) **after catalysis** for Mo (left) and V (right). Note, that the POMs were not kept rigorously under air-free conditions post-catalysis and could have partially oxidized V.

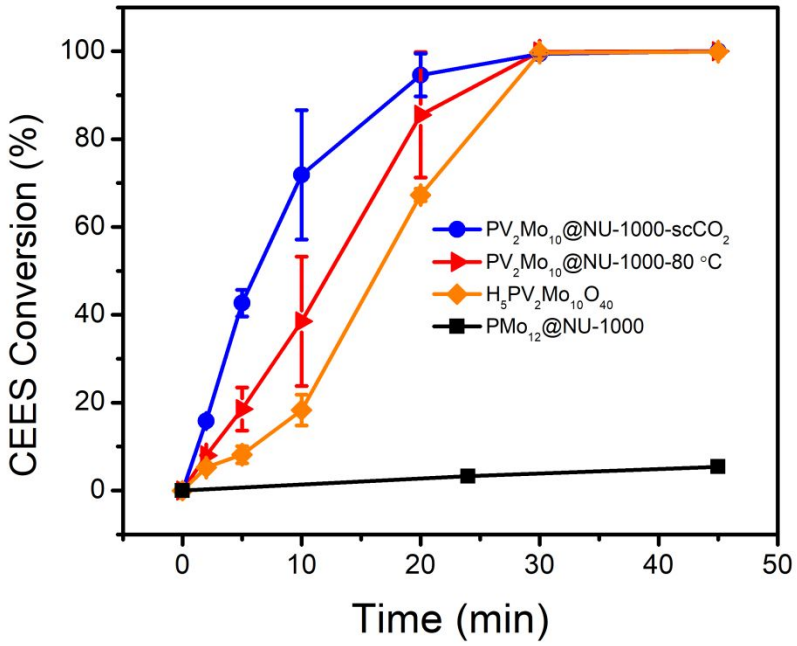

Figure S9. The kinetic traces with error bars of each material used for reaction (Figure 3A). Catalyst is normalized to the number of POM clusters, the reductant is isobutyraldehyde, 1 mL cyclohexane was used as solvent. Traces are averages of at least 3 trials. Error bars represent 1 standard deviation.

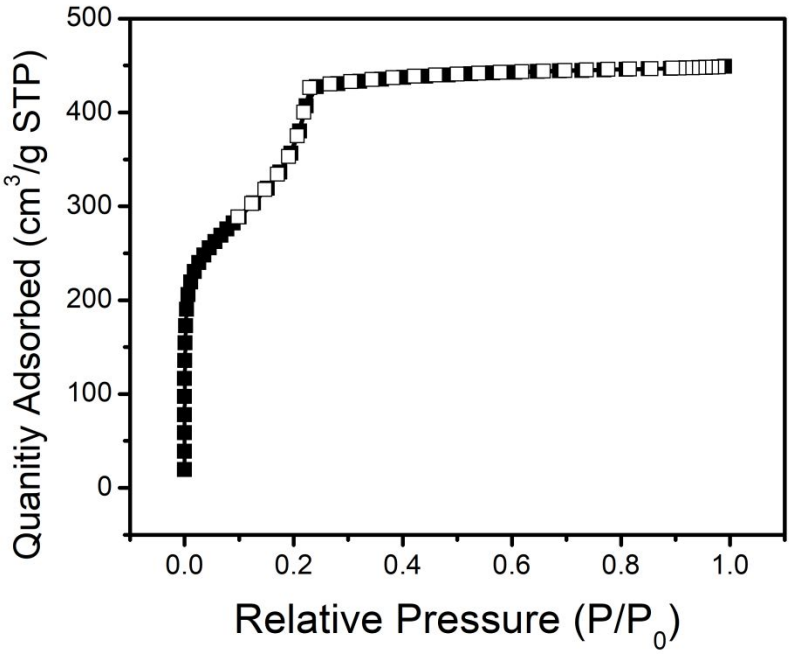

Figure S10. Gravimetric N_2 adsorption (filled) and desorption (unfilled) isotherms for PMo_{12}@NU-1000 after $scCO_2$ activation (BET: 1450 m^2/g).

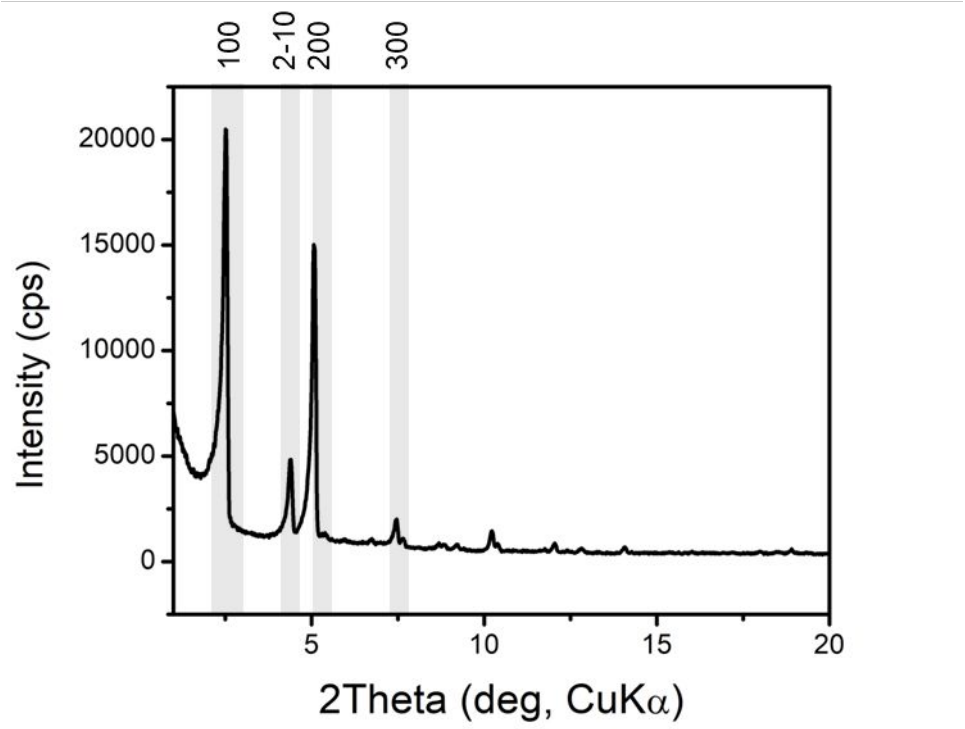

Figure S11. Indexed PXRD pattern for PMo_{12}@NU-1000 after $scCO_2$ activation showing POMs primarily located in micropores.

Table S1. Reaction conditions tuning amount of reductant, temperature, atmosphere, and solvent collected at 45 min.

Catalyst	Reductant	Temperature (°C)	Atmosphere	Solvent	Conversion (%)
$H_5PV_2Mo_{10}O_{40}$	5 eq	70	O_2	Cyclohexane	100
$H_5PV_2Mo_{10}O_{40}$	5 eq	70	**Air**	Cyclohexane	23
$H_5PV_2Mo_{10}O_{40}$	5 eq	70	**N_2**	Cyclohexane	<1
$H_5PV_2Mo_{10}O_{40}$	**2 eq**	70	O_2	Cyclohexane	27
$H_5PV_2Mo_{10}O_{40}$	**1 eq**	70	O_2	Cyclohexane	3
$H_5PV_2Mo_{10}O_{40}$	**0 eq**	70	O_2	Cyclohexane	1
$H_5PV_2Mo_{10}O_{40}$	5 eq	**22**	O_2	Cyclohexane	14
$H_5PV_2Mo_{10}O_{40}$	5 eq	70	O_2	**Acetonitrile**	9
$H_3Mo_{12}O_{40}$	5 eq	70	O_2	Cyclohexane	4
NU-1000	5 eq	70	O_2	Cyclohexane	<1
PMo_{12}@NU-1000	5 eq	70	O_2	Cyclohexane	5
PV_2Mo_{10}@NU-1000-scCO_2	5 eq	70	O_2	Cyclohexane	100
PV_2Mo_{10}@NU-1000-80°C	5 eq	70	O_2	Cyclohexane	100
Recycled PV_2Mo_{10}@NU-1000	5 eq	70	O_2	Cyclohexane	100
Recycled $H_5PV_2Mo_{10}O_{40}$	5 eq	70	O_2	Cyclohexane	5

Section S4. References

(1) Nelson, A. P.; Farha, O. K.; Mulfort, K. L.; Hupp, J. T. Supercritical Processing as a Route to High Internal Surface Areas and Permanent Microporosity in Metal - Organic Framework Materials. *J. Am. Chem. Soc.* **2009**, *131*, 458–460.

(2) Farha, O. K.; Shultz, A. M.; Sarjeant, A. A.; Nguyen, S. T.; Hupp, J. T. Active-Site-Accessible, Porphyrinic Metal À Organic Framework Materials. *J. Am. Chem. Soc.* **2011**, *133*, 5652–5655.

(3) Shultz, A. M.; Farha, O. K.; Adhikari, D.; Sarjeant, A. A.; Hupp, J. T.; Nguyen, S. T. Selective Surface and Near-Surface Modification of a Noncatenated, Catalytically Active Metal-Organic Framework Material Based on Mn(salen) Struts. *Inorg. Chem.* **2011**, *50*, 3174–3176.

(4) Silversmit, G.; Depla, D.; Poelman, H.; Marin, G. B.; De Gryse, R. Determination of the V2p XPS binding energies for different vanadium oxidation states (V5+ to V0+). *J. Electron Spectros. Relat. Phenomena* **2004**, *135* (2–3), 167–175.

(5) Choi, J.-G.; Thompson, L. T. XPS study of as-prepared and reduced molybdenum oxides. *Appl. Surf. Sci.* **1996**, *93* (2), 143–149.