SUPPORTING INFORMATION

Metal–Organic-Framework-Supported and -Isolated Ceria Clusters with Mixed Oxidation States

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Materials

Zirconvl chloride octahvdrate. 1,3,6,8-tetrabromopyrene, (4-(methoxycarbonyl)phenyl)boronic acid, K₃PO₄, hydrochloric acid, hydrogen peroxide, benzoic acid and sodium borohydride (powder, ≥98.0%) were purchased from Sigma Aldrich Chemicals Company, Inc. (Milwaukee, WI) and were used as received. The NU-1000 ligand, 1.3.6.8-tetrakis(p-benzoic acid)pyrene (H₄TBAPy), was synthesized based on our previous procedures.¹ Concentrated sulfuric acid was purchased from VWR Scientific. LLC (Chicago, IL). The compound tetrakis(2,2,6,6-tetramethyl-3,5heptanedionato)cerium(IV) (Ce(tmhd)₄) and tris(i-propylcyclopentadienyl)cerium(III) (Ce(iPrCp)₃) were obtained from Strem Chemicals and used without further purification. Cerium and zirconium ICP standards were purchased from Sigma-Aldrich (St. Louis, MI). Acetone, chloroform, N,N-dimethylformamide (DMF), anhydrous toluene and dimethyl 4nitrophenyl phosphate (DMNP) were obtained from Sigma Aldrich and used without further purification. Deuterated dimethylsulfoxide DMSO (d₆), and deuterated sulfuric acid D₂SO₄ (d₂) were obtained from Cambridge Isotope Laboratory. Ultrapure deionized water (18.2 MB•cm resistivity) was obtained from a Millipore Milli-Q Biocel A10 instrument (Millipore Inc., Billerica, MA).

Material Synthesis

Synthesis of NU-1000. The MOF NU-1000 was synthesized through a slightly modified procedure from literature, which is detailed below.² A screw cap jar (1.0 L) was charged with $ZrOCl_2 \cdot 8H_2O$ (4.85 g, 27.3 mmol), benzoic acid (135.0 g, 1.1 mol) and 300 mL DMF, forming a suspension, which was subjected to sonication until it became clear. Separately, a sample of H₄TBAPy (2.0 g, 3.0 mmol) and 100 mL of DMF were added to a 250 mL screw cap jar, resulting in a yellow suspension. Both jars were subsequently incubated in a 100 °C oven for 1 h, after which time both solutions were combined together in the 1 L screw cap jar. It was then placed in a 120 °C oven for 16 h. The mother liquor was decanted while it was still hot. DMF (250 mL) was added to the reaction container to wash the sample and the yellow crystalline samples were harvested via centrifugation. This procedure was repeated three times with a time interval of 15 min between each wash with DMF.

Activation of NU-1000. The as-synthesized NU-1000 was suspended with 400 mL of DMF in a screw cap jar (1.0 L), in which 25 mL of 8 M HCl solution was added. It was then placed in a 120 °C oven for 16 h. The mother liquor was decanted while it was still hot. An amount of 250 mL fresh DMF was added to the jar for washing purposes and the yellow crystalline samples were then harvested via centrifugation. This procedure was repeated three times with a time interval of 15 min between each wash. It was then suspended in 400 mL DMF for 8 h, after which time the washing procedure was repeated with 250 mL acetone three times. Subsequently, the samples were suspended in acetone for 24 h. NU-1000 was obtained via centrifugation and placed in a vacuum oven set at 100 °C for an hour before it was heated under a dynamic vacuum at 120 °C for 24 h.

Synthesis of Ce-I/n-SIM-NU-1000. In an Ar-filled glovebox, activated NU-1000 (50 mg, 0.023 mmol) was added to a VWR microwave vial charged with 20 mL anhydrous toluene containing either tris(i-propylcyclopentadienyl)cerium(III) (130 mg, 0.28 mmol), or tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)cerium(IV) (245 mg, 0.28 mmol), respectively. It was sealed and then transferred out of the glovebox and heated at 80 °C for overnight under air/water-free conditions. After cooling to room temperature, the vial was transferred back to the glovebox where the solid material was washed ×3 with 3 h of soaking time in between each wash using toluene. Then, it was transferred out of the glovebox and to do x3 solvent exchange using acetone before placing it into a vacuum oven at 100 °C for an hour. Water pulses step was performed in ALD chamber under 120 °C overnight to remove the residual precursor ligands. Each of its pulses follows the time sequence of t1-t2-t3, where t1 is the water pulse time, t2 the exposure time, and t3 the N2 purge time (t1 = 0.015 s, t2 = t3 = 300 s). The powder was then isolated and thermally activated under dynamic vacuum on a Smart VacPrep (120 °C, 12 h). The recovered material, denoted as Ce-X-SIM-NU-1000, was kept in a vacuum desiccator for storage.

Synthesis of Ce-I/n-SIM-NU-1000-R. The activated Ce-X-SIM-NU-1000 (10 mg) was added to a VWR microwave vial, sealed and maintained under N_2 gas environment. In another VWR microwave vial, it was charged with the sodium borohydride solution containing 5 mL of anhydrous methanol and 15 mg of sodium borohydride powder. The sodium borohydride solution was then transferred to Ce-X-SIM-NU-1000 vial and kept stirring for 1 hour under N_2 atmosphere. After the solid settled down, the upper solution was removed and the solid material was washed 3x with 1 h of soaking time in between each wash using anhydrous methanol. The powder was then isolated and thermally activated under vacuum oven (80 °C) overnight. The recovered material, named as Ce-X-SIM-NU-1000-R, was kept in a vacuum desiccator for storage.

Characterization Methods

X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy (XPS) measurements were carried out at the KECKII/NUANCE facility at NU on a Thermo Scientific ESCALAB 250 Xi (Al K α radiation, hv = 1486.6 eV) equipped with an electron flood gun. XPS data was analyzed using Thermo Scientific Avantage Data System software and all spectra were referenced to the C1s peak (284.8 eV).

Powder X-ray Diffraction. Powder X-ray Diffraction (PXRD) data were collected at the IMSERC X-ray Facility at Northwestern University on a STOE-STADI-MP powder diffractometer equipped with an asymmetric curved Germanium monochromator (CuK α 1 radiation, $\lambda = 1.54056$ Å) and one dimensional silicon strip detector (MYTHEN2 1K from DECTRIS). The line focused Cu X-ray tube was operated at 40 kV and 40 mA. Powder was packed in a 3 mm metallic mask and sandwiched between two layers of polyimide tape. The instrument was calibrated against a NIST Silicon standard (640d) prior the measurement. Measurements were made over the range 2°<20<10° with a 0.05° step width and a 4°/min scanning speed.

 N_2 Adsorption and Desorption Isotherms. N_2 adsorption and desorption isotherms were measured on a Micromeritics Tristar II 3020 (Micromeritics, Norcross, GA) instrument at 77 K. Pore-size distributions were obtained using DFT calculations using a carbon slit-pore model with a N_2 kernel. Before each run, samples were activated at 120 °C for 12–24 h under high vacuum on a Smart Vacprep from Micromeritics. Around 30–50 mg of sample was used in each measurement and the BET surface area was calculated in the region P/P₀ = 0.005–0.05.

Inductively-coupled Plasma Optical Emission Spectroscopy. Inductively coupled plasma optical emission spectroscopy (ICP–OES) was conducted in the Quantitative Biological Imaging Center (QBIC) at Northwestern University on a Varian Vista-MDX model ICP-OES spectrometer (Varian, Walnut Creek, CA) equipped with a CCD detector and an argon plasma to cover the 175–785 nm spectral range. Samples (2–3 mg) were digested in a small amount (1 mL) of a mixture of 3:1 v/v conc. H_2SO_4 : H_2O_2 (30 wt % in H_2O) by heating in a Biotage (Uppsala, Sweden) SPX microwave reactor (software version 2.3, build 6250) at 150 °C for 5 minutes. The acidic solution was then diluted to a final volume of 15 mL with ultrapure deionized H_2O and analyzed for Ce (404.076 and 535.353 nm) and Zr (339.198, 343.823, and 349.619 nm) content as compared to the standard solutions.

Scanning Electron Microscopy. Scanning electron microscopy (SEM) images were collected on a Hitachi SU8030 FE-SEM (Dallas, TX) microscope at Northwestern University's EPIC/NUANCE facility. Samples were activated and coated with OsO_4 to ~ 9 nm thickness in a Denton Desk III TSC Sputter Coater (Moorestown, NJ) before imaging.

Synchrotron X-ray Scattering and Pair Distribution Function Analysis. High energy X-ray scattering was performed at sector 11-ID-B at the Advanced Photon Source at Argonne National Laboratory using 58.7 keV ($\lambda = 0.2113$ Å) X-rays. Samples were loaded into 0.5 mm kapton capillaries and placed in a multi-sample stage at a sample-to-detector distance of 20 cm, calibrated using crystalline CeO₂ powder. Geometric corrections and reduction to one-dimensional data was performed using GSAS-II. Pair distribution function (PDF) analysis was performed on 1-D diffraction data within PDFgetX2.² Differential pair distribution functions (dPDFs) were generated by scaling and subtracting the PDF of pristine NU-1000 with no guest present from the PDF of Ce-I/n-SIM-NU-1000. Calculated PDFs were determined using PDFgui.³

Synchrotron X-ray Diffraction and Difference Envelope Density Analysis. High resolution X-ray diffraction data for difference envelope density analysis (DED) were collected on the 11-ID-B beamline at the Advanced Photon Source at Argonne National Laboratory using 58.7 keV ($\lambda = 0.2113$ Å) X-rays. Data were collected using an amorphous silicon-based area detector. For powder diffraction analysis, data were collected with a long sample-to-detector distance (95 cm, calibrated using crystalline CeO₂ powder) to maximize the resolution of the powder pattern. Geometric corrections and reduction to one-dimensional data was performed using GSAS-II. Lattice parameters and peak intensities were extracted from diffraction patterns *via* Le Bail whole pattern fitting⁴ using Jana 2006⁵ based on the reported structure of NU-1000 (P₆/mmm, $a \sim 39$ Å, $c \sim 16$ Å).⁶

Lattice and pseudo-Voigt profile parameters were refined over a $0.2-11.5^{\circ} 2\theta$ range. Structure envelopes were generated using the intensities of ten low index reflections.⁷⁻⁸ Difference envelope densities were then obtained by subtraction of the envelope for pristine NU-1000 from the envelope of Ce-I/n-SIM-NU-1000.

Catalytic Hydrolysis Measurements. Hydrolysis profiles were recorded by in-situ ³¹P NMR measurement at 25 °C. Ce-I/n-SIM-NU-1000(-R) catalysts (1.95 mg, 3 mol%, 0.75 μ mol Zr₆) and NU-1000(-R) catalysts (1.65 mg, 3 mol%, 0.75 μ mol Zr₆) were added in a 1.5 dram vial, and 1.05 mL of 0.4 M N-ethylmorpholine solution (0.05 mL N-ethylmorpholine, 0.9 mL DI water and 0.1 mL D₂O) was loaded into the vial and then sonicated for 1 min to disperse the MOF powder, to which 4 μ L of DMNP (25 μ mol) was added and swirled for 15 s. The reaction mixture was then transferred to an NMR tube and the spectra were instantly recorded; the first data point was collected ~2-3 min after the beginning of the reaction. The progress of the reaction was monitored with 1 min increments for 1 h (number of scans = 16, delay time = 28 s).

Figures



Figure S1. Powder X-ray diffraction pattern of Ce-I/n-SIM-NU-1000-R as compared to NU-1000-R.



Figure S2. SEM/EDS line scan of Ce-l/n-SIM-NU-1000 materials indicating the uniform deposition of Ce ions throughout the crystals. (a) NU-1000; (b) Ce-l-SIM-NU-1000; and (c) Ce-n-SIM-NU-1000 (scale bar inside the images is 10 μ m).



Figure S3. XPS spectra of Zr3d scan on (a) as-synthesized Ce-I/n-SIM-NU-1000 and (b) Ce-I/n-SIM-NU-1000-R.



Figure S4. SEM/EDS line scan of Ce-I/n-SIM-NU-1000-R materials indicating the uniform deposition of Ce ions maintains throughout the crystals after reduction. (a) NU-1000-R; (b) Ce-I-SIM-NU-1000-R; and (c) Ce-n-SIM-NU-1000-R (scale bar inside the images is 10 μ m).



Figure S5. SEM image and SEM-EDS line scans of Ce-I/n-SIM-NU-1000 after hydrolysis catalysis (scale bar inside the images is $10 \mu m$).



Figure S6. Powder X-ray diffraction patterns of post-hydrolysis Ce-l/n-SIM-NU-1000 and Ce-l/n-SIM-NU-1000-R materials.



Figure S7. Superimposed pairs of XPS spectra of Ce-SIM samples with different Ce³⁺ fractions.

Tables

Table S1.

	Ce Loading	Ce ³⁺ Atomic Percentage	Hydrolysis Half-life
Materials	(per Zr ₆ node)	(%)	(min)
NU-1000-R	N/A	N/A	15
Ce-I-SIM-NU-1000-R	2.1 (2.0)	6	7
Ce-n-SIM-NU-1000-R	2.7 (2.6)	21	14

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