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Supporting Information

Heterobimetallic Metal-Organic Framework Nanocages as Highly Efficient Catalysts for CO₂ Conversion under Mild Conditions

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Table of contents

| | Captions | | |
|-------------------------|--|-----|--|
| Chemicals | | S4 | |
| Characterization | | S5 | |
| Synthesis of Au/Phen | | S6 | |
| Fig. S1 | Nitrogen adsorption-desorption isotherms of ZIF-8 (triangles) and Au/Zn-MOF nanocage (cycles). | S7 | |
| Fig. S2 | The TEM and HRTEM image of RH Au/Zn-MOF nanocage after etching for 18 h (a,b). | S8 | |
| Fig. S3 | Kinetic profiles of the framework metal ion exchange of Zn^{2+} with Au^{3+} from ZIF-8 structure. | S9 | |
| Fig. S4 | XRD patterns of ZIF-8 and RD Au/Zn-MOF nanocage. | S10 | |
| Fig. S5 | (a) XRD pattern of RH Au/Zn-MOF nanocage and RD Au/Zn-MOF nanocage catalyst after being reused for 6 times. (b) TEM image of RH Au/Zn-MOF nanocage catalyst after being reused for 6 times. (c) TEM image of RD Au/Zn-MOF nanocage catalyst after being reused for 6 times. | S11 | |
| Fig. S6 | Energy dispersive spectroscopic for RH Au/Zn-MOF nanocage. | S12 | |
| Fig. S7 | XPS spectra of (a) Zn LM2 and (b) N 1S that are obtained from ZIF-8 (black) and Au/Zn-MOF (red). | S13 | |
| Fig. S8 | Schematic illustrations and corresponding TEM images of a rhombic dodecahedron. | S14 | |
| Fig. S9 | (a) TEM image of an individual RD Au/Zn-MOF nanocage. (b) HAADF-STEM image of an individual RD Au/Zn-MOF nanocage. (c) cross-sectional compositional line profiles of RD Au/Zn-MOF nanocage recorded along the line marked in panel b. | S15 | |

| Fig. S10 | TEM images of the samples obtained at six representative stages during the evolution process from polyhedra to nanocage. | S16 |
|--------------------------|--|---------|
| Scheme S2 | Proposed mechanism for cycloaddition of epoxides with CO_2 catalyzed by Au/Zn-MOF. | S17 |
| Tab. S1 | Comparison with other MOF-based catalytic systems on cycloaddition reaction of CO_2 to propylene oxide. | S18,S19 |
| Supporting references | | S20 |

Chemicals

The following chemicals were obtained as indicated: Zinc nitrate hexahydrate $(Zn(NO_3)_2 \cdot 6H_2O, 99.0\%, Sigma-Aldrich)$, 2-methylimidzole (MIM, 99%, Sigma-Aldrich), Sodium tetrachloroaurate (NaAuCl₄, 99.0%, Tianjin Guangfu Company), Methanol (Tianjin Guangfu Fine Chemical Research Institute), Tetrabutylammonium iodide (TBAI) (Sigma-Aldrich), Acetone and ethanol (absolute for analysis, 99.9%, Tianjin Guangfu Fine Chemical Research Institute). All the chemicals are reagent-grade and used as received. High-purity water (18.25 M Ω ·cm) supplied by a UP Water Purification System was used in all the experiments.

Characterization

Morphology of the samples was characterized with a transmission electron microscope (TEM) system (JEOL Model JEM-2100F) operating at 200 kV. The crystal phase of samples was investigated using a Bruker D8 Advance diffractometer X-ray diffraction (XRD) operating at 40 kV and 40 mA equipped with a nickel-filtered Cu K α radiation (λ =1.54056 Å). X-ray photoelectron spectroscopy (XPS) data were obtained on a PHI-1600 instrument equipped with Al K α radiation. Element composition was analyzed using a VISTA-MPX EL02115765 inductive coupled plasma optical emission spectrometer. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption/desorption measurement (Quantachrome Instruments, Micrometrics TriStar 3000).

Synthesis of Au/Phen

Sodium tetrachloroaurate (65 mg) and 1,10-phenanthroline (Phen) (60 mg) were dissolved in 3.0 mL and 1.0 mL of acetone with stirring, respectively. Then the sodium tetrachloroaurate solution was added dropwise to the 1,10-phenanthroline solution with stirring, forming a yellow precipitate, and the mixture was kept stirring for 8 h at room temperature. The precipitate was separated by centrifugation, dried at 60 °C under vacuum for 8 h to yield Au/Phen as a yellow solid.



Scheme S1. Synthesis of Au/Phen.

Figures and Tables



Figure S1. Nitrogen adsorption-desorption isotherms of ZIF-8 (triangles) and Au/Zn-MOF nanocage (cycles).



Figure S2. The TEM and HRTEM image of RH Au/Zn-MOF nanocage after etching for 18 h (a, b).



Figure S3. Kinetic profiles of the framework metal ion exchange of Zn^{2+} with Au^{3+} from ZIF-8 structure.



Figure S4. XRD patterns of ZIF-8 and RD Au/Zn-MOF nanocage.



Figure S5. (a) XRD pattern of RH Au/Zn-MOF nanocage and RD Au/Zn-MOF nanocage catalyst after being reused for 6 times. (b) TEM image of RH Au/Zn-MOF nanocage catalyst after being reused for 6 times. (c) TEM image of RD Au/Zn-MOF nanocage catalyst after being reused for 6 times.



Figure S6. FT-IR spectra of ZIF-8, Au/Zn-MOF nanocage and Au/Zn-MOF nanocage catalyst after being reused for 6 times.



Figure S7. 13C-CP-MAS NMR spectra of activated ZIF-8 and Au/Zn-MOF.



Figure S8. Energy dispersive spectroscopic for RH Au/Zn-MOF nanocage.



Figure S9. XPS spectra of (a) Zn LM2 and (b) N 1S that are obtained from ZIF-8 (black) and Au/Zn-MOF (red).



Figure S10. Schematic illustrations and corresponding TEM images of a rhombic dodecahedron.



Figure S11. (a) TEM image of an individual RD Au/Zn-MOF nanocage. (b) HAADF-STEM image of an individual RD Au/Zn-MOF nanocage. (c) cross-sectional compositional line profiles of RD Au/Zn-MOF nanocage recorded along the line marked in panel b.



Figure S12. TEM images of the samples obtained at six representative stages during the evolution process from polyhedra to nanocage.



Scheme S2. Proposed mechanism for cycloaddition of epoxides with CO₂ catalyzed by Au/Zn-MOF.

| Entry | MOF catalyst | Pore (nm) | Reaction conditions | Yields (%) | TOF (h ⁻¹) | Ref. |
|-------|--|-----------|-----------------------------|---------------|---------------------------|--------------|
| 1 | RH Au/Zn-MOF | 0.34 | r.t., 1 atm, 24 h | 83 | 2.5 | This work |
| 2 | RH Au/Zn-MOF | 0.34 | 70 °C, 30 atm, 6 h | 98 | 11.7 | This work |
| 3 | HKUST-1 | 1 | 80 °C, 19.7 atm, 8 h | 5.4 | _ | R1 |
| 4 | MOF-5 | 0.4-0.6 | 80 °C, 19.7 atm, 8 h | 2.5 | _ | R1 |
| 5 | PCN 224 (Co) | 1.9 | 100 °C, 19.7 atm, 4 h | 42 | 115 | R6 |
| 6 | MOF-505 | 0.83 | r.t., 1 atm, 48 h | 48 | _ | 27 |
| 7 | MMCF-2 | - | r.t., 1 atm, 48 h | 95.4 | _ | 27 |
| 8 | $[Zn_6(TATAB)_4(DABCO)_3(H_2O)_3] \bullet$ $12DMF \bullet 9H_2O$ | - | 100 °C, 1 atm, 16 h | 99 | 15 | R2 |
| 9 | BIT-103 | - | 160 °C, 30 atm, 24 h | 95.2 | 9.6 | R3 |
| 10 | BIT-102 | - | 160 °C, 30 atm, 24 h | 89.4 | 9.0 | R3 |
| 11 | BIT-101 | - | 160 °C, 30 | 84.7 | 7.3 | R3 |

Table S1. Comparison with other MOF-based catalytic systems on cycloadditionreaction of CO_2 to propylene oxide.

| | | | atm, 24 h | | | |
|----|---|---------|------------|------|---|----|
| 12 | In ₂ (OH)(btc)(Hbtc) _{0.4} (L) _{0.6} • 3H ₂ O | - | 80 °C, | 93.9 | | |
| | | | 19.7 atm, | | _ | R4 |
| | | | 4 h | | | |
| 13 | UMCM-1-NH ₂ | 1.7-2.8 | r.t., 11.8 | 90 | _ | R5 |
| | | | atm, 24 h | | | |
| 14 | MIL-101-N-(n-Bu) ₃ Br | 1.3-2.7 | 80 °C, | 98.6 | | |
| | | | 19.7 atm, | | _ | R1 |
| | | | 8 h | | | |
| 15 | MIL-101-P(n-Bu) ₃ Br | - | 80 °C, | 99.1 | | |
| | | | 19.7 atm, | | _ | R1 |
| | | | 8 h | | | |

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