Electronic Supporting Information

Cooperative Ion-exchange and Self-redox Process to Load Catalytic Metal Nanoparticles into a MOF with Johnson-type Cages

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Experimental Section

Materials and Instrumentation: All reagents were purchased commercially and used without further purification. The purity of all gases is 99.999%. All syntheses were carried out in a 20 mL vial under autogenous pressure. Diffraction data were collected by using a Oxford SuperNova diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 100 K. The structure was solved by direct methods and refined by the full-matrix least-squares technique by using SHELXTL. All Powder X-ray diffraction (PXRD) analyses were recorded on a Rigaku Dmax2500 diffractometer with Cu K α radiation ($\lambda = 1.54056$ Å) with a step size of 0.05°. Thermal stability studies were carried out on a NETSCHZ STA-449C thermoanalyzer with a heating rate of 10 °C/min under an air atmosphere. Gas adsorption measurement was performed in the ASAP (Accelerated Surface Area and Porosimetry) 2020 System. All the Gas-chromatography (GC) measurements were analyzed using a GC-9790 II (China) with a CP8751 capillary column (L = 30 m; ID = 0.25 µm) and aflame ionization detec-tor (FID). Analysis of noble metal content was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an Ultima 2 analyzer (Jobin Yvon). X-ray photoelectron spectra (XPS) were acquired with a PHI Quantum 2000 XPS system with a monochromatic Al K α source and a charge neutralizer.

Synthesis of $[Zn_{17}thb_{14}(\mu_4-O)_4(H_2O)(Me_2NH_2)]\cdot Me_2NH_2$ (1): 2,5-thiophenedicarboxylate acid (H₂thb, 103 mg, 0.6 mmol) and Zn(NO₃)₂·6H₂O (293 mg, 1 mmol) were dissolved in 4 mL N,N-dimethylacetamide (DMA) and 1 mL methanol (MeOH). The mixture was placed in a small vial and heated at 100 °C for 3 days, and then cooled to room temperature. Colorless block crystals of the product were formed and collected by filtration and washed with DMA several times. Yield: ~160 mg (~72% based on H₂thb).

X-ray Crystallography: Diffraction data for **1** was collected on a Saturn 70 charge-coupled device diffractometer equipped with confocal-monochromated Mo-Ka radiation ($\lambda = 0.71073$ Å) at 100 K. The Crystal Clear program was used for absorption correction. The structure was solved by direct methods and refined on F^2 by full-matrix, least-squares methods using the SHELXL-97 program package. The total interstitial solvent molecule contents were determined by TGA.

Crystal data of 1: tetragonal, a = 24.429(5) Å, c = 45.411(11) Å, V = 27100(10) Å³, T = 293(2) K,

space group *I4/mmm*, Z = 4, 86165 reflections measured, 6555 independent reflections ($R_{int} = 0.0721$). The final R_I values were 0.0939 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.2989 ($I > 2\sigma(I)$). The goodness of fit on F^2 was 1.100.

Hydrogenation of styrene and filtration test: Hydrogenation of styrene was carried out in solution under hydrogen atmosphere (1 bar) at 303 K. In a typical reaction, 50 mg of dried M@1 were placed in a 25 mL Schlenk flask and then vacuumized for 10 min. 5.00 g styrene (48 mmol, precursor catalyst to substrate weight ratio 1:100) were added and the mixture was stirred under hydrogen-bubbling at corresponding temperature and time. 20 µL of the reaction mixture was acquired at corresponding test time, and then dissolved in 1 mL ethanol solution to track the conversion of styrene using gas chromatograph. For the filtration test, the reaction mixture was filtered off after 3 h using a 0.45 µm PTFE filter. The catalyst was separated and the solution was allowed to react further in a second vial under the same reaction conditions.



Figure S1. The novel (4,6)-connected net with Schlafli symbol $\{3^2 \cdot 4^8 \cdot 5^3 \cdot 6^2\}_4 \{3^4 \cdot 4^2\}$ of 1



Figure S2. Viewing along a and b directions, the 3D supramolecular architecture of **1** originated from the stacking of infinite layers in an ABAB fashion.



Figure S4. PXRD patterns of the simulsted one (a), 1 (b), 1-ht (c), Pd@1 (d), Ag@1 (e) and Pd@1 after catalysis (e).

Thermal gravimetric analysis (TGA), X-ray powder diffraction (XRPD) experiments were carried out to examine the stability of the framework. The TGA curve of **1** shows a continual weight loss without an obvious plateau from 25 to 500 °C (Figure S3a, ESI). By soaking **1** in CH₂Cl₂ for 5 days, the TGA of CH₂Cl₂-exchanged sample (**1a**) shows a weight loss of 29.8% before 150 °C and subsequently a steady plateau from ~150 to ~250 °C, indicating that all original guest molecules in the cages can be completely exchanged by CH₂Cl₂ (Figure S3b, ESI). For gas adsorption studies, **1a** was evacuated under high dynamic vacuum at room temperature for 24 hours, forming the active phase **1-ht**. The PXRD patterns compare of **1** and **1-ht** confirm that integrity of the framework is maintained without some broad peaks maybe induced by the slight relax of the open framework (Figure S4a-c, ESI).



Figure S6. BET surface areas calculated from the range identified through the consistency criteria and accessible surface area.



Figure S7. The photos of 1 (left), 1b (middle) and Pd@1 (right).



Figure S8. Energy dispersive X-ray spectrum (EDS) for Pd@1.



Figure S9. Energy dispersive X-ray spectrum (EDS) for Ag@1.



Figure S10. The repeated process for Pd@1 under 60 °C.



Figure S11. The recycling test for Pd@1 under 60 °C.



Figure S12. H¹-NMR measurement in trifluoroacetic acid-D for 1a.



Figure S13. Images for a large single crystal of Pd@1 (a) and its cross-section (b).