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Mechanochemistry-assisted encapsulation of metal nanoparticles into MOF matrices through a sacrificial strategy

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Electronic Supplementary Information (ESI)

Experimental Section

Materials

ZnO (~20 nm) particles, 2-methyl-imidazol (Hmim), terephthalic acid (ta), 1,4-diaza[2.2.2]bicyclooctane (dabco), 1,3,5-benzenetricarboxylic acid (BTC), $Y_2(CO_3)\cdot xH_2O$, $HAuCl_4\cdot 3H_2O$, 1-hexene, cyclooctene, tetraphenyl ethylene, hex-1,4-diene were purchased from Aladdin, ethyl acetate, n-dodecane, $PdCl_2$, CuO, NH_4Cl, $Cu(NO_3)_2\cdot 3H_2O$, ethanol, N,N-Dimethylformamide (DMF), methanol, styrene, KNO_3, were purchased from Sinopharm Chemical Reagent Co., Ltd. All the chemicals and solvents were used as received without further purification.

Synthesis of Pt@ZIF-8, Ru@ZIF-8.

The synthesis procedure is similar to that of Pd@ZIF-8 except replacement of $PdCl_2$ with $PtCl_2$ (0.038 g) or $RuCl_3$ (0.047 g).

Synthesis of Pd@ $[Zn_2(ta)_2(dabco)]$.

The as-synthesized Pd/ZnO (0.4 g), ta (0.8 g), dabco (0.28 g), KNO_3 (0.2 g), DMF (0.4 mL) were placed into a 50 mL ZrO_2-jar along with 15 g ZrO_2 ball bearings (diameter 5 mm). After grinding for 30 min at a speed of 40 Hz, gray powder was collected, washed with methanol for several times and then dried at 150 ^oC for 12 h.

Synthesis of Au/CuO.

The $Cu(NO_3)_2·3H_2O$ (3 g) and $HAuCl_4·3H_2O$ (0.05 g) were added to a 50 mL ZrO_2-jar along with 15 g ZrO_2 ball bearings (diameter 5 mm). After grinding for 2 h at a speed of 40 Hz, the powder was calcinated at 350 ˚C for 2 h (2 ^oC / min). Then the powder was cooled to room temperature and Au/CuO was obtained.

Synthesis of Au@HKUST-1.

The obtained Au/CuO (0.36 g), BTC (0.64 g), NH_4Cl (0.05 g), ethanol (0.25 mL) and H_2O (0.25 mL) were added to a 50 mL ZrO_2-jar along with 15 g ZrO_2 ball bearings (diameter 5 mm). The mixture was grinded for 30 min at a speed of 40 Hz and aged in the jar for 4 h. The resulting blue sample was collected, washed with ethanol for several times to remove BTC and then dried at 150 ^oC for 12 h.

Synthesis of $Pd/Y_2(CO_3)·xH_2O$

$Y_2(CO_3)·xH_2O$ (1 g) and $PdCl_2$ (0.028 g) were added to a 50 mL ZrO_2-jar along with 15 g ZrO_2 ball bearings (diameter 5 mm) and grinded at a speed of 40 Hz. Then the powder was collected and reduced under H_2 flow at 150 ^oC for 4 h (5 ^oC / min). After cooling to room temperature, the $Pd/Y_2(CO_3)·xH_2O$ was obtained.

Synthesis of $Pd@[Y(BTC)(H_2O)]$.

The obtained $Pd/Y_2(CO_3)·xH_2O$ (0.376 g), BTC (0.42 g) and DMF (0.2 mL) were added to a 50 mL ZrO_2-jar along with 15 g ZrO_2 ball bearings (5 mm). After grinding for 30 min at a speed of 40 Hz, the sample was collected, washed with ethanol for several times to remove BTC, and then dried at 150 ^oC for 12 h.

Scale-up synthesis of Pd@ZIF-8.

The as-synthesized Pd/ZnO (4 g), Hmim (8 g), NH_4Cl (0.50 g) and ethanol (3.25 mL) were added to a 50 mL ZrO_2-jar along with 15 g of ZrO_2 ball bearings (diameter 5 mm). The mixture was grinded for 30 min at a speed of 40 Hz and gray powder was obtained. The gray powder was washed with ethanol for several times to remove Hmim and then dried at 60 °C for 12 h.

For all synthesis, the mechanochemical strategy was performed on a QM-WXO4 ball miller (Nanjing University Instrument Factory).

Characterization of Prepared Samples

The actual metal contents were quantified with an inductively coupled plasma-optical emission spectrometer (ICP-OES) on Agilent Technologies 5100 ICP-OES. Thermal gravimetric analysis (TGA) was the measurement on a Mettler Toledo TGA/DSC 3^+STAR^e system in air. Transmission electron microscopy (TEM) was performed using a JEM-2100 (JEOL Co., Japan) microscope operating at 200 kV to observe the morphology and size distribution of samples. XPS (X-ray photoelectron spectra) were performed on an ESCALAB250Xi (ThermoFisher Scientific) electron spectrometer using Al Ka radiation (1486.6 eV) operated at 12.5 kV and 12 mA. The spectra were obtained at ambient temperature under ultra-high vacuum. During data processing, the binding energy was calibrated with reference to the C 1s peak of the contaminant carbon at 284.6 eV. X-ray diffraction (XRD) data were collected at ambient temperature on a Puxi DX-3 diffractometer using Cu Kα radiation at 40 kV, 40 mA with a scan speed of 1 °/min. The Brunauer-Emmet-Teller surface area (BET) of the catalyst was measured by Autosorb iQ2 analyzer (Quantachrome) at 77 K. Before measurement, the sample was pretreated at 200 °C under high vacuum for 12 h.

Catalytic Activity Measurement

Catalytic hydrogenations of alkene.

The experiment was carried out in a Schlenk tube with alkene (2 mmol), ethyl acetate (EA) (5 mL), n-dodecane (2 mmol) as internal standard substances and catalyst (10 mg). Before each operation, the air in the tube was exchanged by hydrogen for three times. The reaction was proceeded at 1 atm of hydrogen and at 35 °C for 12 h, and the products were detected by using a gas chromatograph coupled with an HP-5 column and a flame ionization detector (Agilent 7820A).

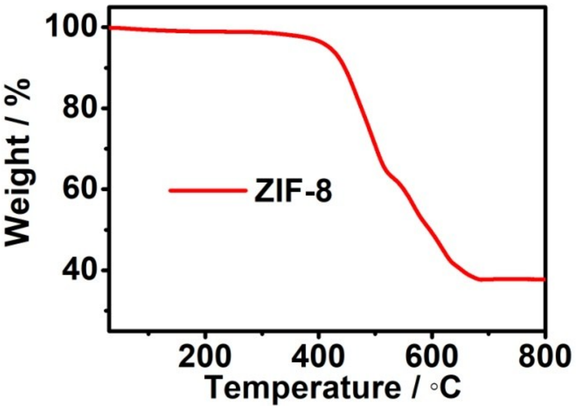

Fig. S1 TGA curve of ZIF-8 synthesized by the mechanochemical method.

Thermogravimetric analysis (TGA) was employed to estimate the Zn yield. The formula of the perfect ZIF-8 is $C_8H_{10}N_4Zn$. Upon heat treatment in air, the ZnO is the final product and the ideal end weight percent should be 35.8%. Fig. S1 presents the TGA curve of ZIF-8 synthesized by the mechanochemical method, and the end weight percent is 37.5%, which is close to the ideal value. This indicates that most of ZnO is converted to the ZIF-8, the yield of ZIF-8 reaches 98.3% based on ZnO.

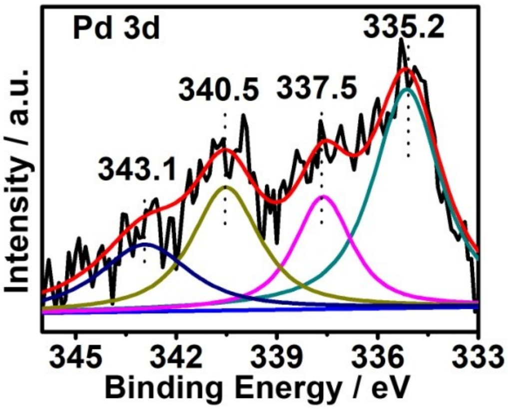

Fig. S2 High resolution of Pd 3d XPS spectra.

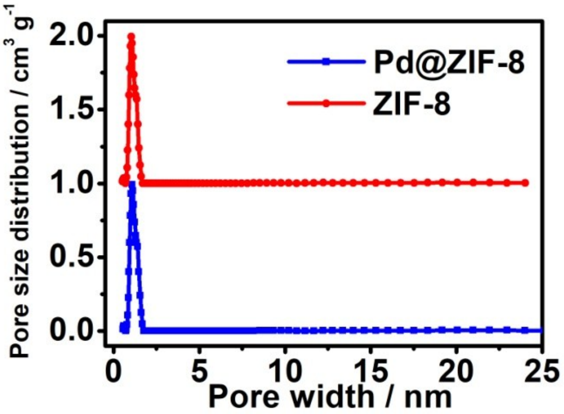

Fig. S3 Pore size distributions of ZIF-8 and Pd@ZIF-8. For clarity, the pore size distribution of ZIF-8 is offset along the y axis by 1.0 cm^3 g^{-1}.

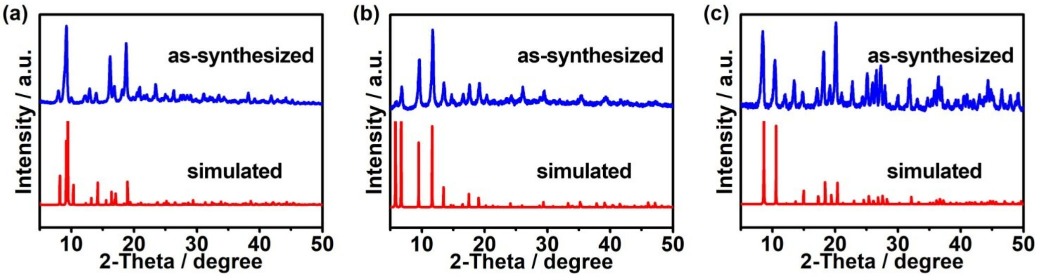

Fig. S4 XRD patterns of (a) Pd@[$Zn_2(ta)_2(dabco)$]; (b) Au@Cu-HKUST; (c) Pd@[Y(BTC)(H_2O)].

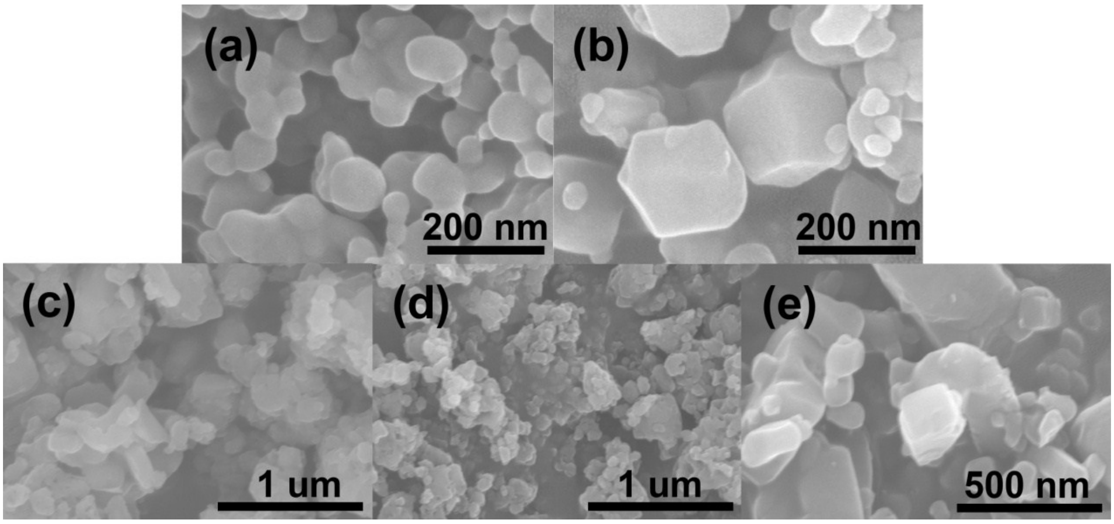

Fig. S5 SEM images of (a) ZIF-8; (b) Pd@ZIF-8; (c) Pd@[$Zn_2(ta)_2(dabco)$]; (d) Au@Cu-HKUST; (e) Pd@[Y(BTC)(H_2O)].

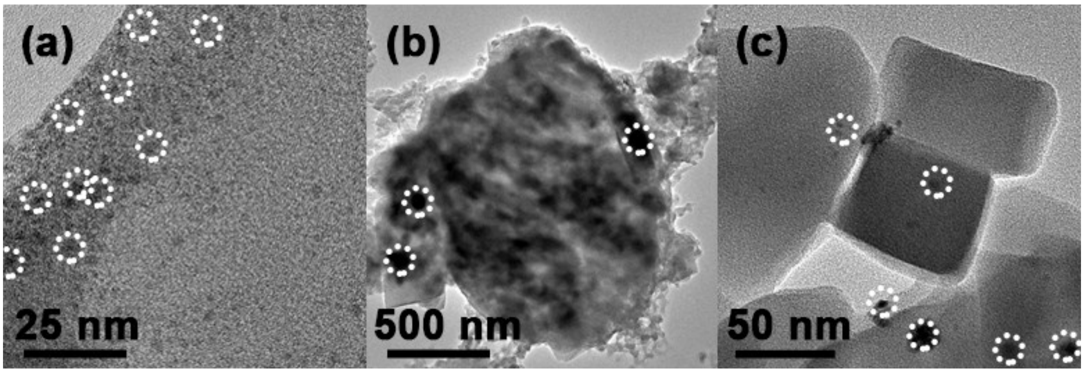

Fig. S6 TEM images of a) Pd@[Zn_2(ta)$_2$(dabco)]; b) Au@Cu-HKUST; c) Pd@[Y(BTC)(H_2O)].

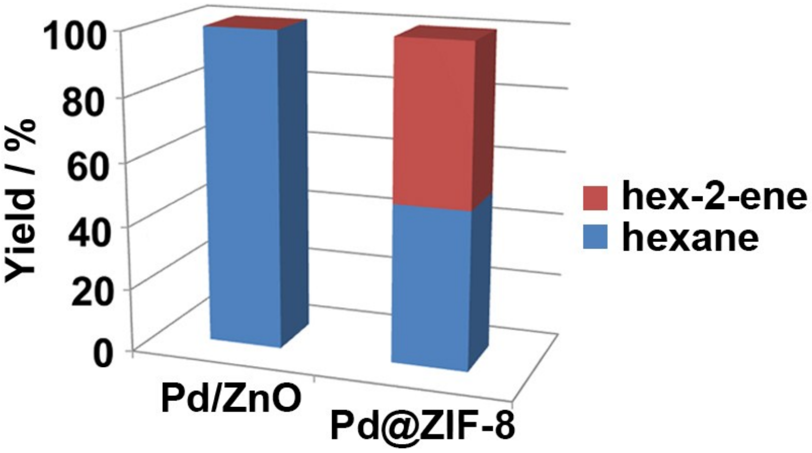

Fig. S7 Site-selective hydrogenation of hex-1,4-diene.

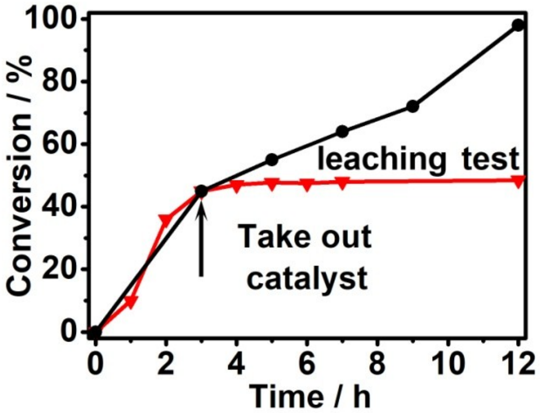

Fig. S8 Leaching test of Pd@ZIF-8 for 1-hexene hydrogenation.

The leaching test was carried out. The Pd@ZIF-8 was separated from the reaction system after 3 h and the reaction continued with the remaining filtrate. As revealed by the Fig. S8, the hydrogenation of 1-hexene immediately stops after removing the catalyst, indicating almost no Pd was leached from the catalyst. This is agreement with the ICP-OES results.

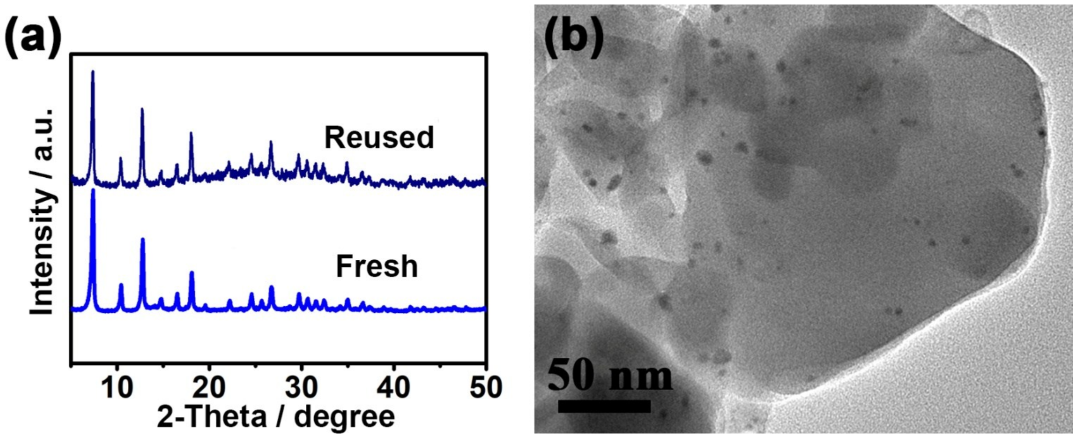

Fig. S9 XRD patterns (a) and TEM image of Pd@ZIF-8 after 5 runs (b).