Electronic supplementary information

ZIF-Derived Porous Carbon Supported Pd Nanoparticles within Mesoporous Silica Shells: Sintering- and Leaching-Resistant Core-Shell Nanocatalysts

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Chemicals and reagents

$Zn(NO_3)_2 \cdot 6H_2O$ (98%, Alfa Aesar), 2-methylimidazole (MeIM, 99%, Acros), Palladium(II) acetylacetonate ($Pd(acac)_2$, Pd 34.7%, Alfa Aesar), N, N-dimethylformamide (DMF, Sinopharm Chemical), methanol (MeOH, Sinopharm Chemical), ethanol (EtOH, Sinopharm Chemical), cetyltrimethylammonium chloride solution (CTAC, 25 wt % in H_2O, Aldrich), tetraethyl orthosilicate (TEOS, ≥99%, Aldrich). All of the chemicals used in this experiment were used as received without any further purification.

Catalyst preparation

Synthesis of Pd^{2+}/ZIF-8 NPs. A predetermined amount of $Pd(acac)_2$ and $Zn(NO_3)_2 \cdot 6H_2O$ were added into in a DMF-MeOH-EtOH (v/v/v = 3:1:1) mixture. And the mixture was treated by ultrasonication for 30 min to form a solution. 2-methylimidazole was dissolved in DMF-MeOH (v/v = 4:1) to generate a clear solution. Then, both solutions were mixed together, and stirred for 24 h at room temperature. The product was collected by centrifugation, washed very carefully with EtOH and dried under a vacuum overnight. The product was named as Pd^{2+}/ZIF-8.

Synthesis of Pd^{2+}/ZIF-8@mesoSiO$_2$. The Pd^{2+}/ZIF-8@mesoSiO$_2$ was prepared according to the following reported method[1]. The obtained Pd^{2+}/ZIF-8 was directly used without any further treatment. Briefly, a certain amount of Pd^{2+}/ZIF-8 and 250 mg of MeIM were dispersed in 33 mL of H_2O and 20 mL of EtOH. After 10 min of ultrasonic treatment, 0.55ml of CTAC was added and stirred for 20 min. Then 0.4 ml TEOS was added and stirred for another 2 h. The product was collected by centrifugation, washed with EtOH and H_2O, and dried under a vacuum overnight. The product was named as Pd^{2+}/ZIF-8@mesoSiO$_2$.

Synthesis of Pd/ZDC@mesoSiO$_2$. The as-prepared Pd^{2+}/ZIF-8@meosSiO$_2$ was transferred to a tube furnace and pyrolysis under atmosphere of argon at 800 °C for 3 h. And the heating rate was set at 5 °C min^{-1}. After that, the materials were cooled down to room temperature naturally. The final product is referred to as Pd/ZDC@mesoSiO$_2$.

Synthesis of Pd/ZDC. Synthesis of Pd/ZDC was similar to that of Pd/ZDC@mesoSiO$_2$ but starting from Pd^{2+}/ZIF-8.

Catalyst characterization

Transmission electron microscopy (TEM) images were performed on a Hitachi H-800 transmission electron microscope. Dark field scanning transmission electron microscopy (DF-STEM) was performed on FEI Tecnai G2 F20 S-Twin high-resolution transmission electron microscope operating at 200kV. The X-ray powder diffraction (XRD) were obtained on a Rigaku RU-200b with Cu Kα radiation (λ =1.5406 Å). The X-ray photoelectron spectroscopy (XPS) was measured by a PHI Quantera SXM system under 3.1×10^{-8} Pa using Al^+ radiation at room temperature.

N_2 adsorption measurements were performed with a Quantachrome Autosorb-1 instrument surface area analyzer at 77K. The Brunauer–Emmett–Teller (BET) method was used to calculate the specific surface area. The micropore and mesopore size distribution porosity was analyzed using the HK method and Barrett–Joyner–Halenda (BJH) method for desorption branch of the isotherms, respectively. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was tested by Thermo Fisher IRIS Intrepid Ⅱ.

Oxidation of benzyl alcohol：

Benzyl alcohol (0.5 mmol) and catalyst (30 mg) were added to 1.0 mL of toluene. The reaction mixture was heated to 100 °C under mild stirring (stirring rate 300 rpm). After 12 h, the reaction completed and the catalyst was separated by centrifugation, washed with ethanol and further dried at 100 °C under vacuum. Each time, the catalyst was treated under the same conditions and used for recyclability tests. The products were determined by a Thermo Fisher gas chromatograph ISQ-TRACE 1300 equipped with a 30 m × 0.25 mm TR-5MS column, and hexadecane as a GC internal standard.

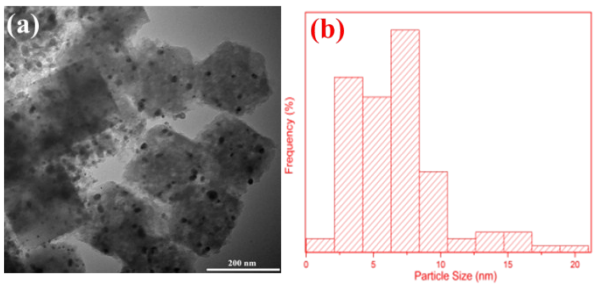

Figure S1. TEM images of (a) Pd/ZDC and (b) Pd NPs size distribution.

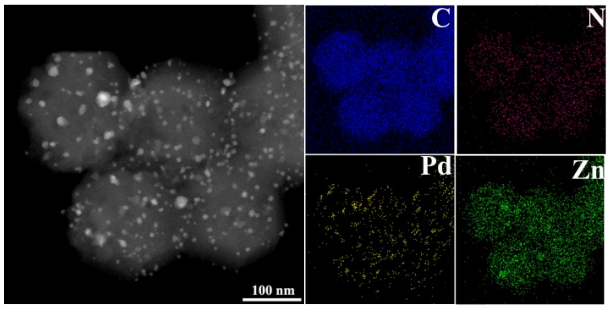

Figure S2. DF-STEM images of Pd/ZDC, corresponding element maps showing the distribution of C (blue), N (purple), Pd (yellow) and Zn (green).

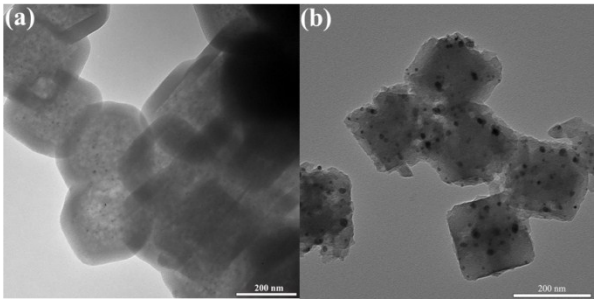

Figure S3. TEM images of (a) Pd/ZDC@meoSiO$_2$ after 8 cycles and (b) Pd/ZDC after 3 cycles.

The Pd loading of the spent Pd/ZDC catalysts is 0.98 wt%. The result shows that Pd loading is decreased by 22.2 percent after only 3 recycles. The TEM image of the spent Pd/ZDC is shown in Fig. S3b. Compared with the TEM image of fresh Pd/ZDC sample (Fig. S1), the number of Pd NPs is going down. These results show that Pd leaching could be avoided efficiently with the protection of the SiO_2 shell.

References

1. Z. Li and H. C. Zeng, *J. Am. Chem. Soc.*, 2014, **136**, 5631-5639.