

Supporting Information

Synthesis of stable heterogeneous catalysts by supporting carbon-stabilized palladium nanoparticles on MOFs

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Experimental Section

Synthesis of ZIF-8: ZIF-8 was synthesized according to the reported method.¹ The synthesis solution with the molar ratio of Zn²⁺ : 2-methylimidazole : H₂O = 1 : 70 : 1238 was prepared as follows. Zn(NO₃)₂·6H₂O (1.17 g, 3.93 mmol) was dissolved in 8 ml deionized (DI) water. 2-methylimidazole (22.70 g, 276.49 mmol) was dissolved in another 80 ml DI water. The zinc nitrate solution was then mixed with the 2-methylimidazole under stirring. After about 5 min continuous stirring, the product was collected by centrifuging, and then washed with DI water for several times. Finally, the product was dried at 65 °C overnight in a drying oven.

Catalysts preparation: 20 μmol PdCl₂ (0.2 mol L⁻¹) was added to the 0 μl and 160 μl glucose solution (100 g L⁻¹), respectively. The as-prepared ZIF-8 was degassed at 120 °C for 3 h before the next use. Then, ZIF-8 (80 mg) was soaked in the mixed solution of glucose and PdCl₂ and stood overnight, in order to fully infiltrate glucose and Pd²⁺ to the pores and/or surround on the surface of ZIF-8. The obtained intermediate material of glucose-Pd²⁺/ZIF-8 was dried in an oven at 80 °C. Then the material was placed in a tube furnace and heated to 300 °C at a ramping rate of 1.5 °C min⁻¹, keeping 300 °C for 2 h under the Ar/H₂ (5%) flow. After cooling down to room temperature, the samples were collected. The different as-prepared samples are denoted as Pd/ZIF-8, C@Pd/ZIF-8.

Catalytic reactions: In a typical experiment, C@Pd/ZIF-8 catalysts (containing 5.0 μmol Pd) were loaded into a stainless steel autoclave equipped with a stirring bar, and the residual air in the reactor was expelled by purging several times with hydrogen. Subsequently, ethanol (15.0 mL) was added to the reactor and the mixture was sonicated for 10 min to afford a homogeneous suspension. A suitable amount of styrene was introduced, and the mixture was sonicated again for 10 min. In addition, the activity of C@Pd/ZIF-8 for other olefins was also investigated, including 1-heptene, cyclohexene, cyclooctene and quinoline. The reactions were carried out at 80 °C under a constant stirring and hydrogen pressure (2.0 MPa). The products of hydrogenation reaction were analysed by using gas chromatograph. The used catalysts were recovered by filtration, thoroughly washed with ethanol, and then reused under the same experimental conditions to estimate its reusability. As control, the hydrogenation reactions were also conducted using Pd/ZIF-8 (5.0 μmol Pd) under the same experimental conditions.

Characterization: The powder X-ray diffraction (PXRD) patterns were recorded with a Bruker AXS D8 Advance diffractometer using nickel-filtered Cu Kα radiation (λ=1.5406 Å). 2θ angles were scanned from 5° to 50°. Fourier transform infrared (FT-IR) spectroscopy absorption spectra were obtained on a PerkinElmer Frontier instrument, with samples being dispersed on potassium bromide pellets. Thermogravimetric analysis (TGA) was performed on a Q500 analyzer. Scanning electron microscopy (SEM) observations were carried out on a JEOL JSM-7600F field emission scanning electron microscope at 5 kV after sputtering Pt particles on sample surfaces. Transmission electron microscopy (TEM) images were taken on a JEOL JEM-2010F microscope operated at 200 kV. The analyses of the substrate and products were performed with a GC (Agilent, 7890A) equipped with a chromatographic column HP-5. The Brunauer-Emmett-Teller (BET) surface areas were determined in a Micromeritics ASAP Tri-star II 3020 adsorption apparatus at 77 K. Prior to the measurement, the samples were first degassed at 120 °C under vacuum for 12 h.

References

1. Y. Pan, Y. Liu, G. Zeng, L. Zhao and Z. Lai, *Chem. Commun.*, 2011, **47**, 2071.

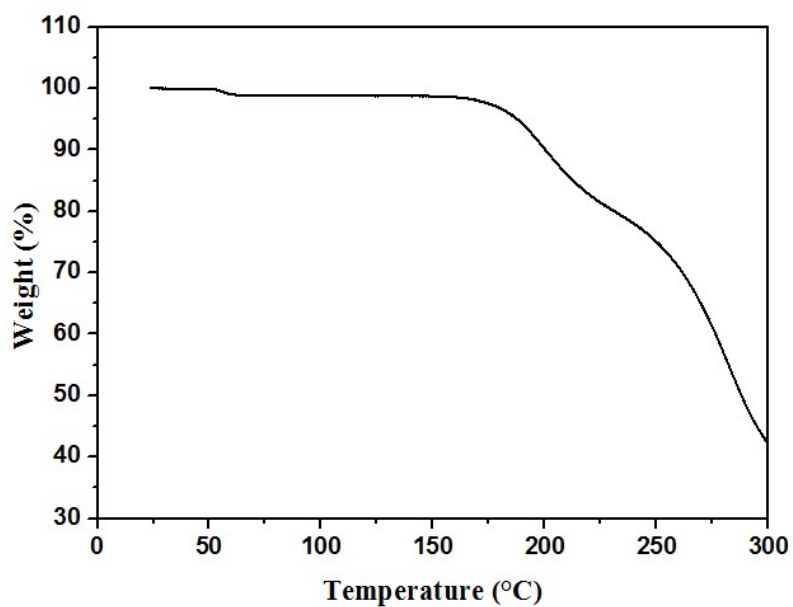


Fig. S1 TGA analysis of D-glucose in N₂ flow.

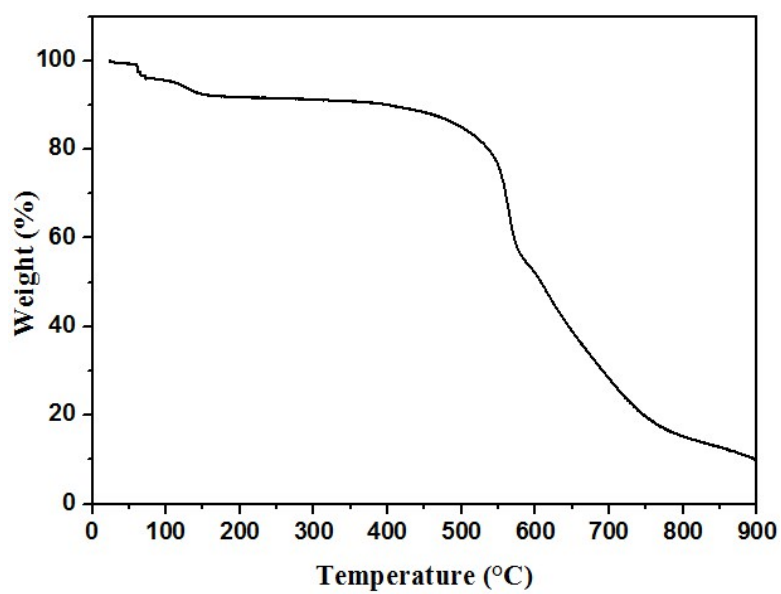


Fig. S2 TGA analysis of the as-prepared ZIF-8 in N₂ flow.

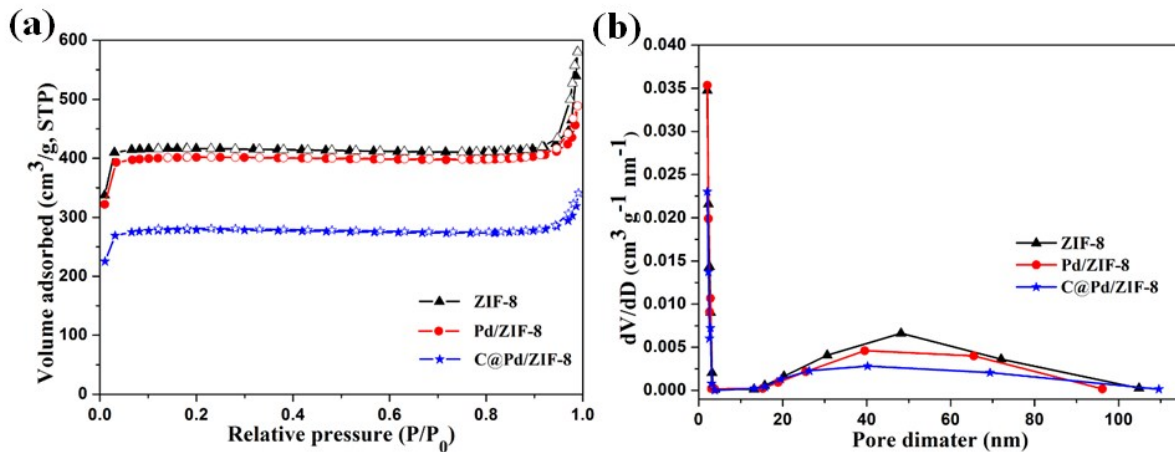


Fig. S3 (a) Nitrogen sorption isotherms of as-prepared ZIF-8, Pd/ZIF-8 and C@Pd/ZIF-8 samples at 77 K. Solid symbols denote adsorption and open symbols denote desorption. (b) The pore size distribution of as-prepared ZIF-8, Pd/ZIF-8 and C@Pd/ZIF-8 samples

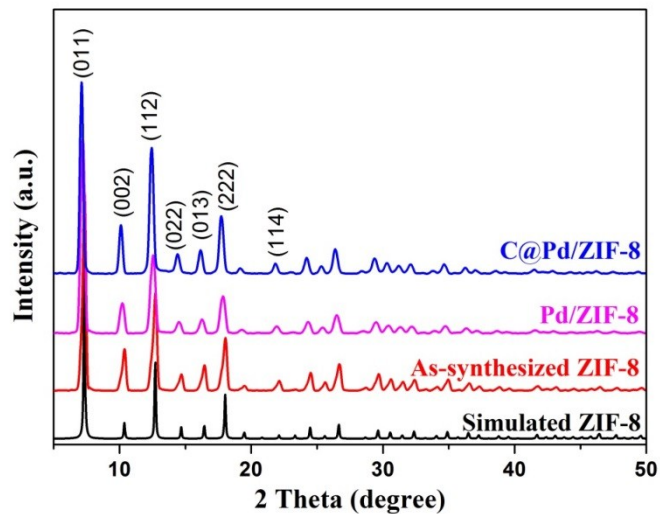


Fig. S4 XRD patterns of the simulated ZIF-8 (black), as-prepared ZIF-8 (red), Pd/ZIF-8 (pink) and C@Pd/ZIF-8 (blue).

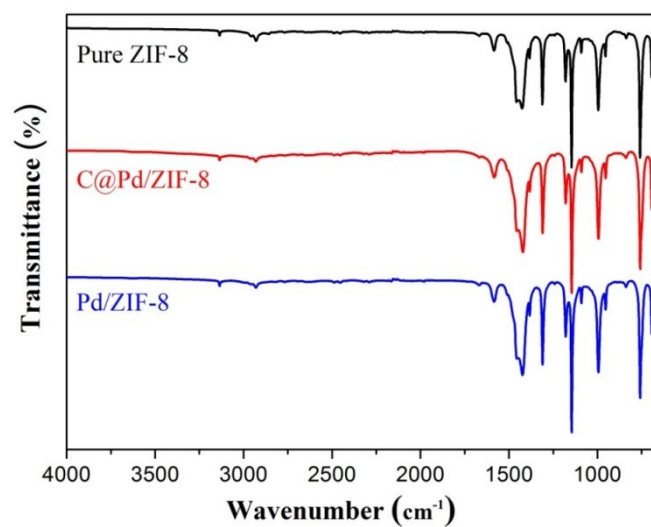


Fig. S5 FT-IR spectra of pure ZIF-8, C@Pd/ZIF-8 and Pd/ZIF-8 catalysts.

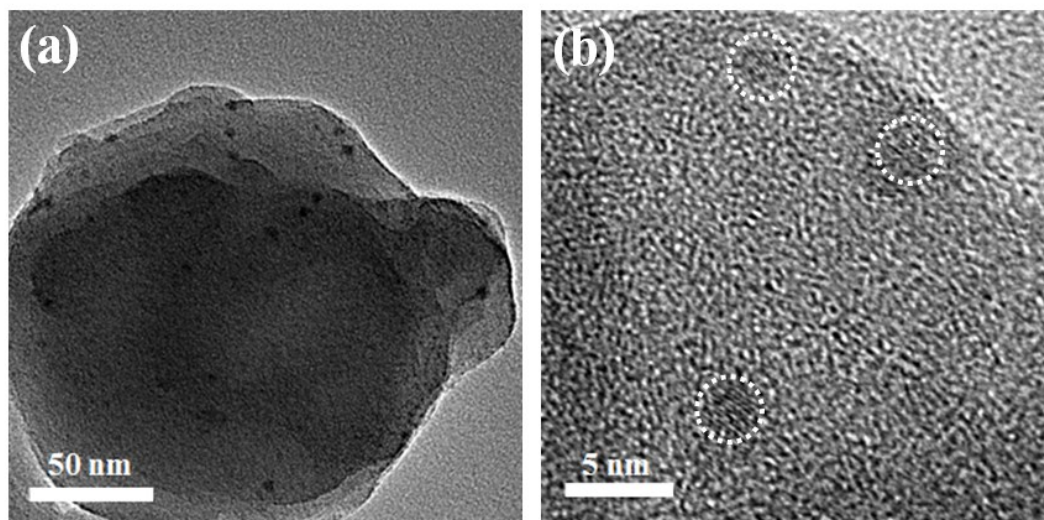


Fig. S6 TEM (a) and HRTEM (b) images of the C@Pd/ZIF-8 used after fifth-run reaction.

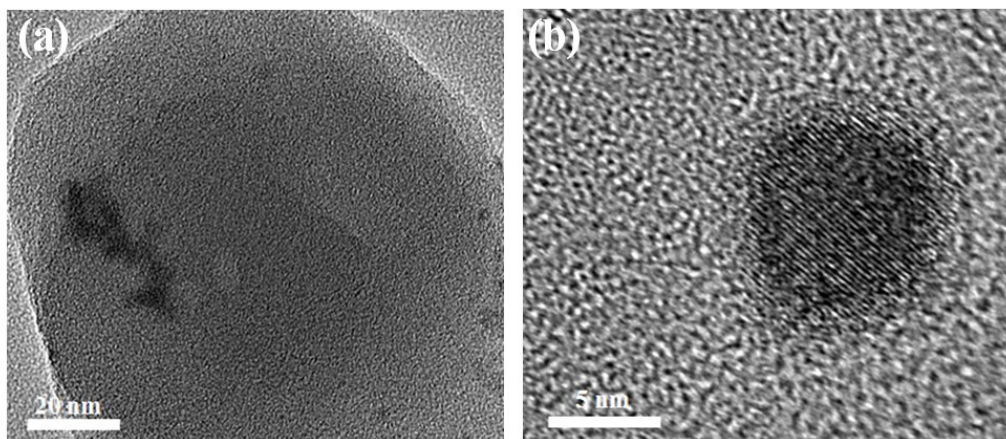
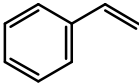
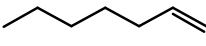



Fig. S7 TEM (a) and HRTEM (b) images of the Pd/ZIF-8 used after fifth-run reaction.

Table S1 Comparison of the cycling stability of the C@Pd/ZIF-8 and Pd/C catalysts in heterogeneous hydrogenation ^a

Cycle	Substrate conversion (%)		
			
1	95.1 ^b (99.9 ^c)	75.2 (81.2)	47.3 (53.2)
2	94.5 (70.5)	74.4 (53.3)	45.1 (37.9)
3	92.7 (45.3)	72.7 (27.6)	42.2 (24.3)
4	87.2 (21.7)	68.3 (11.2)	39.7 (15.5)
5	85.3	66.9	37.5

^a Reaction conditions: 5.0 μmol Pd catalyst, 2.0 MPa H_2 , 80 $^\circ\text{C}$, 30 min, and substrate 2.0 mmol.

^b Results obtained from the C@Pd/ZIF-8 catalyst.

^c Results obtained from the Pd/C catalyst.