Electronic Supplementary Information

Synthesis Procedure

PVP-Pd colloid

0.034 g $PdCl_2$ and 0.3011 g KBr were dissolved in 6 mL of H_2O. 0.1068 g PVP and 0.0619 g ascorbic acid were dissolved in 5 mL H_2O. The former two kinds of solution were mixed in a 50 mL three-neck flask and stirred at 100 ^oC for three hours. The obtained colloid was washed by acetate and chloroform for several times for removing the extra PVP in the solution. The final products were dispersed in 10 mL ethanol.

PVP-Pd@ZIF-8

11.35 g 2-methy imidazole and the previous PVP-Pd colloid ethanol solution (2.5 mL, 10 mL and 20 mL) were dissolved in 40 mL H_2O. Then a H_2O solution of $Zn(NO_3)_2.6H_2O$ (4 mL) was added to the former solution under stirring. The mixture was stirred for extra 90 min at 25 ^oC, after which the black powder was collected by centrifugalization. The products were washed by H_2O (2 times) and methanol (2 times). After drying in vacuum at 120 ^oC for 12 h, the 0.3wt%PVP-Pd@ZIF-8, 1.0wtPVP-Pd@ZIF-8 and 5wt%PVP-Pd@ZIF-8 were obtained.

Catalytic Test

The catalysts were reduced at 200 ^oC for 1.5 h under the atmosphere of $Ar:H_2=2:1$. The freshly reduced catalyst (0.1 g) was mixed with the reactants of BYD (0.568 g) and the internal standard of 1,2-propylene glycol in 10 mL H_2O. The mixture was charged in a 50 mL batch reactor. After the reactor was flushed with H_2 for 3 times, catalytic hydrogenation was conducted under certain H_2 pressure and temperature.

Blank Test

Blank test proceeded in a regular catalytic test procedure at 50 ^oC and 2 MPa H_2

with pure ZIF-8 as catalyst. And less than 2% conversion was obtained, indicating ZIF-8 was inactive for the hydrogenation of BYD.

Characterization

PXRD was carried out using a D/MAX 2400 diffractometer with Cu Kα manochromatized radiation source (λ=1.5418 Å) operated at 40 kV and 100 mA. FT-IR spectra were collected at room temperature on a Nicolet Impact 410 with a resolution of 4 cm^{-1}. The surface area, pore volume, and pore size distribution of ZIF-8 support and Pd@ZIF-8 catalysts were determined from nitrogen adsorption-desorption isotherms at -196 ℃ using a Quantachrome Autosorb-IQ apparatus. The particle size and distribution of the samples were analyzed by TEM (Philips CM200, 120 kV). Powder samples were ultrasonicated in ethanol and dispersed on copper grids. Element analysis was performed on ICP-AES (Perkin-Elmer Optima 2000 DV).

XRD Patterns of ZIF-8 and PVP-Pd@ZIF-8 Catalysts

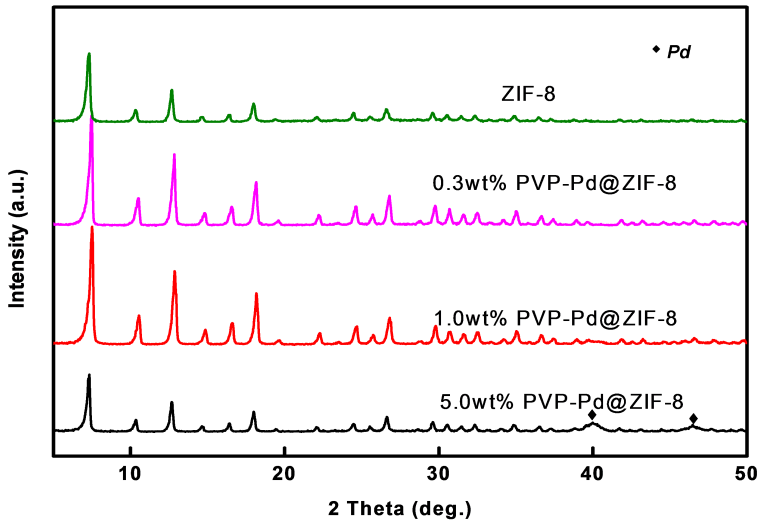


Fig. S1 XRD pattern of ZIF-8 and PVP-Pd@ZIF-8 catalysts.

Thermogravimetric Analysis

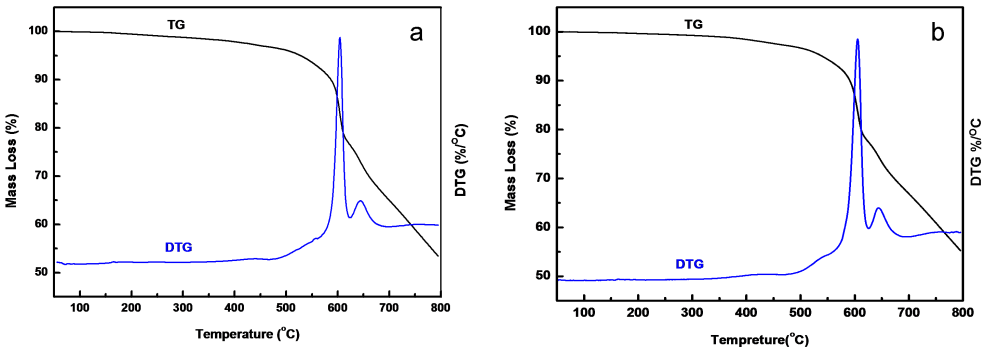


Fig. S2 TG and DTG curves of ZIF-8 (left) and 1.0 wt% PVP-Pd@ZIF-8 (right).

Thermogravimetric analysis of pure ZIF-8 demonstrated that ZIF-8 sample began to decompose at ~500°C. 1.0 wt% PVP-Pd@ZIF-8 composite showed slightly higher weight loss than ZIF-8 for the existence of PVP and Pd. The above results proved the high thermal stability of ZIF-8 and PVP-Pd@ZIF-8 composites.

SEM Images

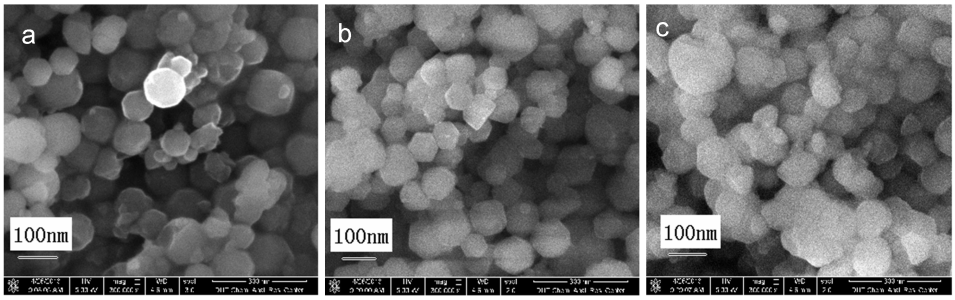


Fig. S3 SEM images of ZIF-8 (a), 1wt%PVP-Pd@ZIF-8 (b) and 1wt%PVP-Pd@ZIF-8 after reaction (c).

Reaction Data

Table S1. Reaction data for linear and ring molecules for 1.0wt% PVP-Pd@ZIF-8

Reactants	Temperature (^{o}C)	H_2 Pressure (MPa)	Time (h)	Conversion (%)
cyclooctene	60	2	4	3.6
n-hexylene	60	2	4	>99
cinnamyl aldehyde	60	2	4	3.7
crotonaldehyde	60	2	4	81.1

The catalyst had a high activity for the linear reactants such as n-hexylene and crotonaldehyde. At the same time, the ring reactants can barely be converted at the same condition. The results indirectly proved that most of the Pd particles are encapsulated by ZIF-8.

Table S2. A summary of literature on hydrogenation of butynediol to butenediol

Catalyst used	Conversion (%)	Selectivity (%)	Condition	Reference
$Pd/CaCO_3$ + lead acetate	52	Mixture	285-289K	1
Pd-Pb-Cd	89	Mixture	423K, 1.5MPa	2
Ru catalyst	-	Mixture	353K, 2.5MPa	3
$Pd/Zn/CaCO_3$	100	99	303-353K, 0.8-3.5MPa	4
Pd/TiO2-additives	83	99	298K	5
Pd-Pb	30	97	298K	6
Pd/C	100	60-75	303-333K	6
Pd/ACF(activated carbon fibers)	100	~70	303K, 0.6MPa	7
$Pt/CaCO_3$	78	73	393K, 1MPa	8
Pd/Resin	100	90	293K, 0.1MPa	9
Bio-Pd	75	98	313K, 0.2MPa	10
Bio-Pt	100	70	313K, 0.2MPa	11
Pt-Bi/C	25	90	313K, 0.2MPa	11

Kinetic Data

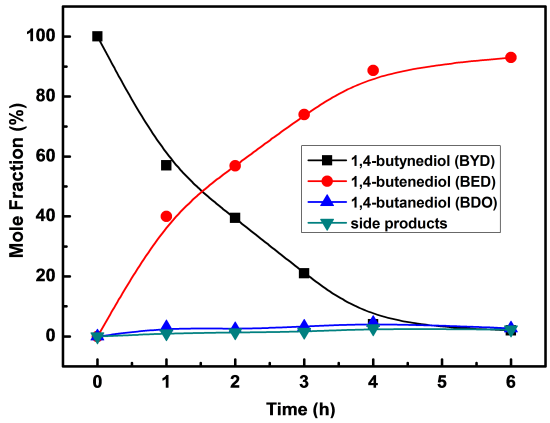


Fig. S4 Kinetic data for 1,4-butynediol hydrogenation for 1wt% Pt@ZIF-8 at 120 ^{o}C and 3 MPa.

N_2 Physisorption Results

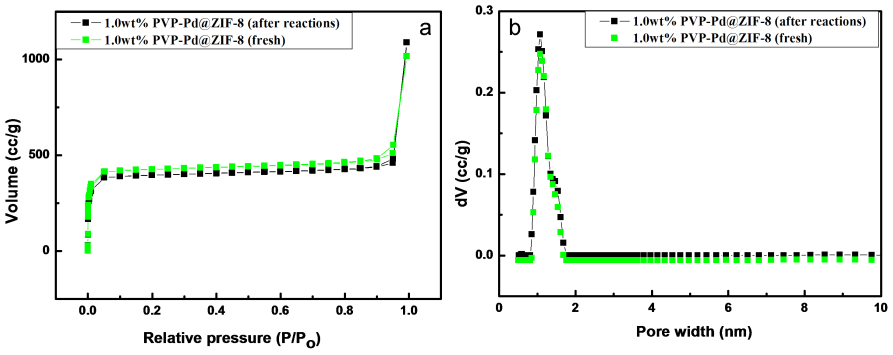
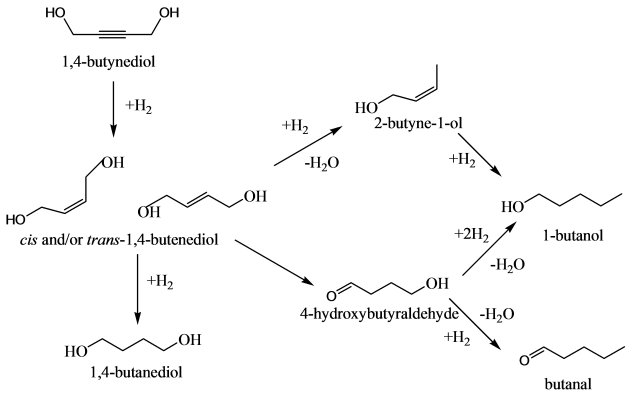


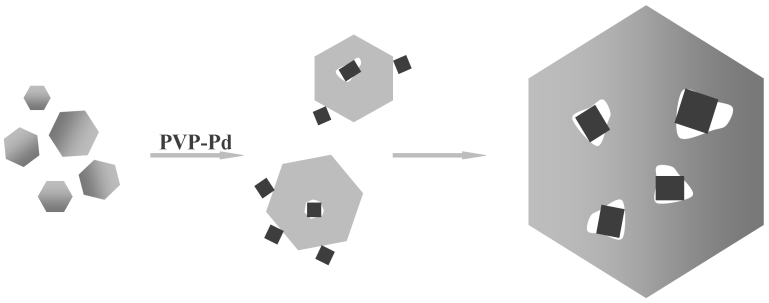
Fig. S5 Nitrogen adsorption isotherms (a) and pore distribution (b) of 1.0wt% PVP-Pd@ZIF-8 before and after reaction.

Reaction Pathway



Scheme S1 Reaction pathway for BYD hydrogenation.

Synthetic Process



Scheme S2 Schematic illustration of preparation of PVP-Pd@ZIF-8 catalysts.

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