

Supplementary Information For

Synergistic Local Hydrogen Confinement and Spillover over Pd@ZIF-8-AT Enables Mild-Condition Hydrogenation of Dicyclopentadiene

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1. Experimental section

1.1 Chemicals

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99.9%) and palladium acetate ($\text{Pd}(\text{OAc})_2$, 99%, Pd \geq 47%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. 2-Methylimidazole (2-MI) was purchased from Anhui Zesheng Technology Co., Ltd. Pentamminotetrazole (5-AT) was purchased from Shanghai Shenzhe Chemical Technology Co., Ltd. Methanol (MeOH, 99%) was purchased from China National Pharmaceutical Group Corporation.

1.2 Hydrogen spillover mechanism test

Disperse 10 mg of catalyst and 100 mg of WO_3 in 20 mL of deionized water. Sonicate briefly, then transfer to a hydrogenation reactor. Maintain at 30°C and 0.5 MPa for 30 minutes.

2 Results and Discussion

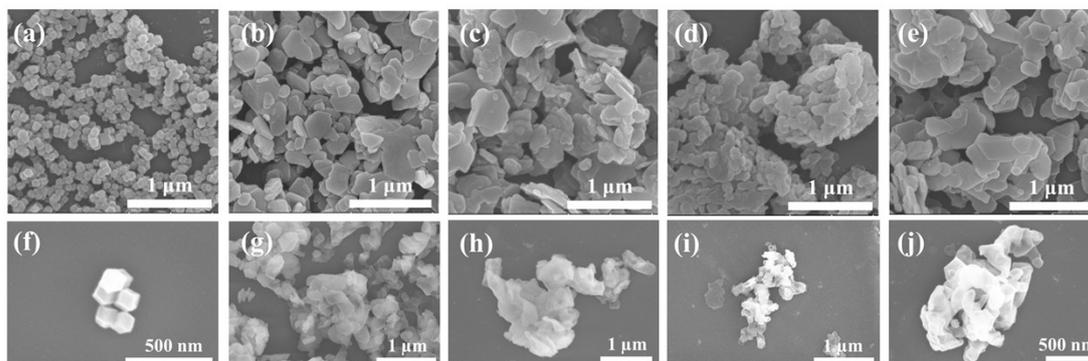


Figure S1. SEM image of ZIF-8-AT-5/0 (a); 4/1 (b); 1/1 (c); 1/4 (d); 0/5 (e); and Pd@ZIF-8-AT-5/0 (f); 4/1 (g); 1/1 (h); 1/4 (i); 0/5 (j).

Table S1. The surface area, and pore volume of ZIF-8-AT-5/0, ZIF-8-AT-4/1, ZIF-8-AT-1/1, ZIF-8-AT-1/4, ZIF-8-AT-4/1, ZIF-8-AT-0/5, and Pd@ ZIF-8-AT-5/0, Pd@ ZIF-8-AT-4/1, Pd@ ZIF-8-AT-

Sample	Surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})	Pore size (nm)
ZIF-8-AT-5/0	1499.89	0.943	2.94
ZIF-8-AT-4/1	508.23	0.799	2.46
ZIF-8-AT-1/1	484.35	0.475	2.39
ZIF-8-AT-1/4	462.15	0.527	2.52
ZIF-8-AT-0/5	287.462	0.301	2.34
Pd@ZIF-8-AT-5/0	1126.4	0.698	2.85
Pd@ZIF-8-AT-4/1	412.65	0.426	3.59
Pd@ZIF-8-AT-1/1	324.3	0.329	2.73
Pd@ZIF-8-AT-1/4	424.816	0.450	3.06
Pd@ZIF-8-AT-0/5	223.64	0.17	2.14

1/1, Pd@ ZIF-8-AT-1/4, Pd@ ZIF-8-AT-0/5.

Table S2. Conversion rates of different samples at 30 °C, 1MPa, 10 min.

Sample	Con-DCPD-1	Con-DCPD-2	Con-DCPD-3
Pd@ZIF-8-AT-5/0	18.4	17.9	18.9
Pd@ZIF-8-AT-4/1	100	100	100
Pd@ZIF-8-AT-1/1	100	100	100
Pd@ZIF-8-AT-1/4	100	100	100
Pd@ZIF-8-AT-0/5	100	100	100

Table S3. Pd content before and after 10 cycles of ZIF-8.

Sample	Pd (wt%)
Before 10 cycles	0.72
After 10 cycles	0.65

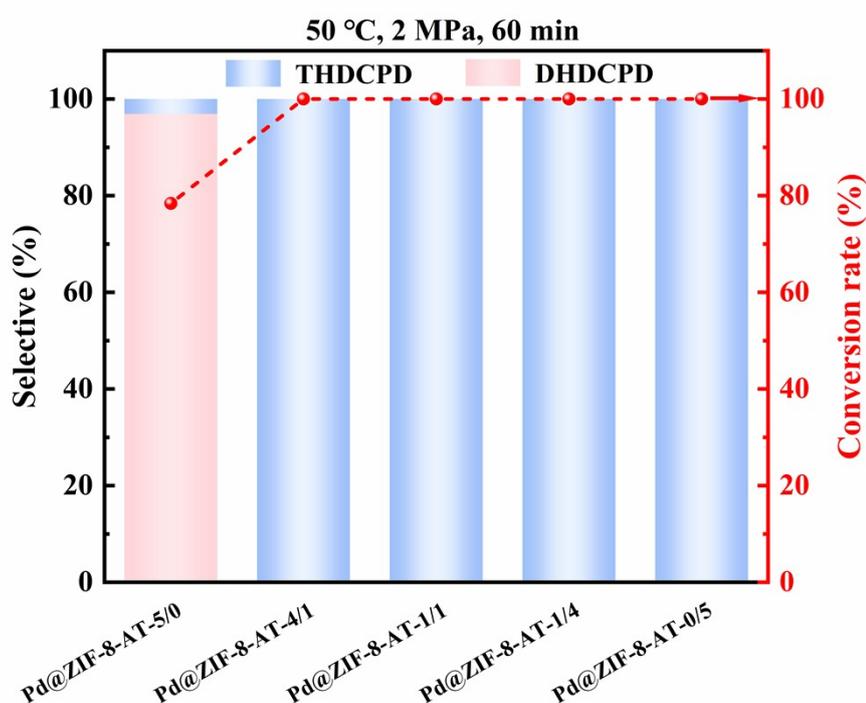


Figure S2. The DCPD hydrogenation of Pd@ZIF-8-AT-5/0, Pd@ZIF-8-AT-4/1, Pd@ZIF-8-AT-1/1, Pd@ZIF-8-AT-1/4 and Pd@ZIF-8-AT-0/5.

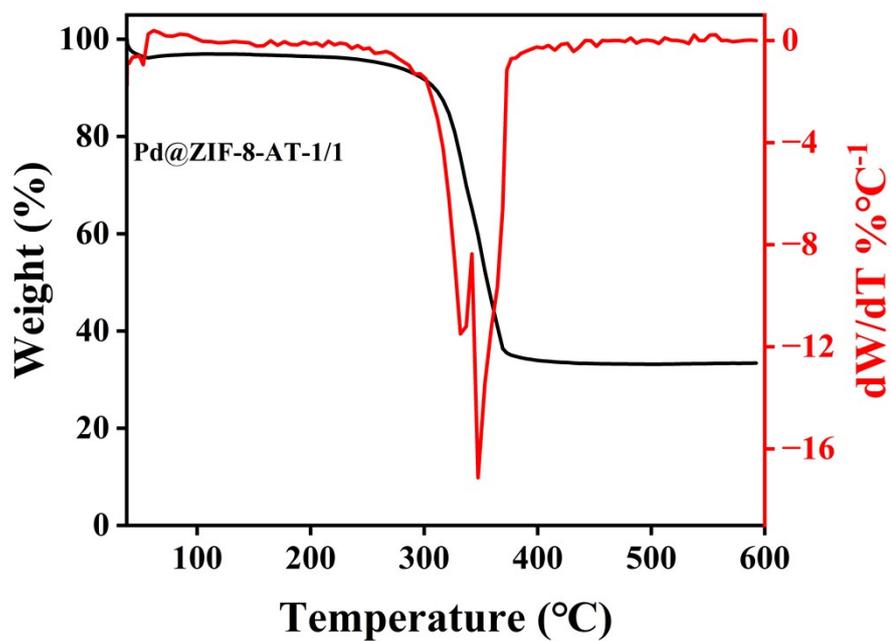


Figure S3. TG curves of Pd@ZIF-8-AT-1/1.

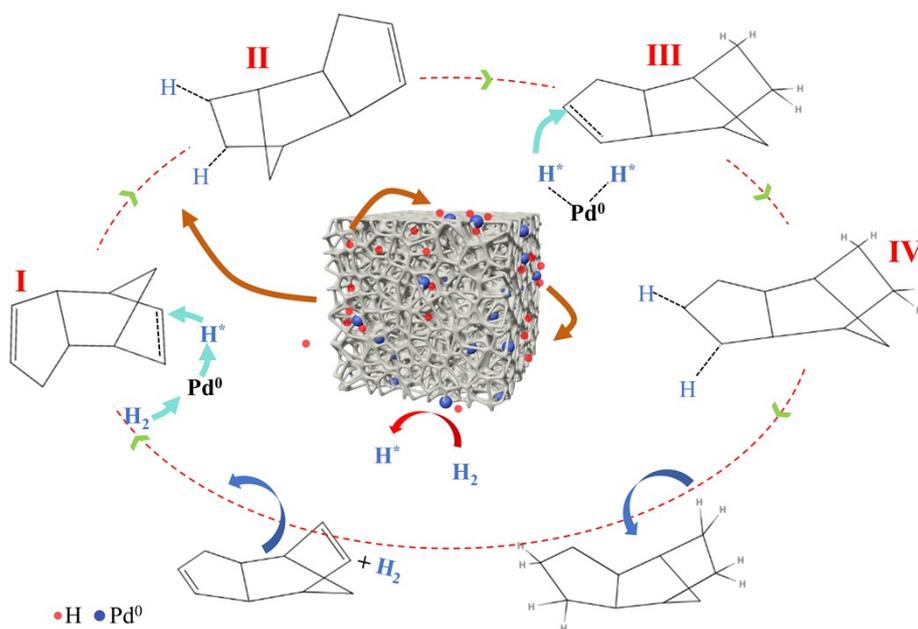


Figure S4. Proposed mechanism for DCPD hydrogenation on Pd@ZIF-8-AT.