Electronic Supporting Information

Zeolitic Imidazolate Framework-8 Templated Synthesis of Heterogeneous Pd Catalyst for Remediation of Chlorophenols Pollutions

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Experimental

Materials. $Zn(NO_3)_2 \cdot 6H_2O$, 2-methylimidazole, $PdCl_2$, $NaBH_4$, 4-CP, 2,4-DCP, 2,4,6-TCP and other chemicals were all analytical reagents and purchased from Aladdin cooperation (China). The commercial activated carbon supported Pd (Pd/AC) catalyst used was purchased from Aladdin cooperation (China), in which the content of Pd was 5 wt%.

Synthesis of Pd/NMC. Zeolitic imidazolate framework-8 (ZIF-8) was synthesized according to the reported method.[1] The synthesized ZIF-8 was degassed at 80 ^oC for 10 h. 100 mg of above ZIF-8 was immersed in the mixed solution of D-glucose (20 mg) and Pd^{2+} ($PdCl_2$ 40 μmol) with stirring overnight, and then dried in an oven at 80 ^oC. Then, the obtained intermediate of D-glucose-Pd^{2+}/ZIF-8 was heated to 550 ^oC in a tube furnace with a heating rate of 1.5 ^oC min^{-1}, and kept at 550 ^oC for 2 h under the Ar/H_2(5%) flow. The nitrogen-doped mesoporous carbon embedded with Pd nanoparticles (Pd/NMC) was obtained after cooling down.

Characterization. Fourier transform infrared spectroscopy (FT-IR) analyses were tested by Lambda 950 NIR spectrophotometer. The morphology of the Pd/NMC catalyst was observed by scanning electron microscopy (SEM, JSM-7600F) and transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN). Powder X-ray diffraction (XRD, Rigaku D/max-2400) measurements were performed in a diffractometer using the Cu-Kα radiation as the X-ray source within the 2θ range of 5-90^o. The Brunauer-Emmett-Teller (BET) surface areas were determined in a Micromeritics ASAP Tri-star II 3020 adsorption apparatus at 77K. Prior to the measurement, the samples were first degassed at 200 ^oC under vacuum for 12 h. Thermogravimetric analysis (TGA, PerkinElmer TGA 8000) was raised from 30 ^oC to 800 ^oC at 5 ^oC min^{-1} in N_2 atmosphere.

Catalytic experiments. In a typical HDC reaction, Pd/NMC (15 mg, Pd content, 5.23 wt%), H_2O (30.0 mL), NaOH (1.5 mmol, 3.0 mmol, 4.5 mmol) and 1.5 mmol of CPs (4-CP, 2,4-DCP or 2,4,6-TCP) were mixed in a 50.0 mL three-necked flask. A balloon filled with H_2 was connected to the flask, and the air in the flask was replaced by H_2 for three times. Subsequently, the reaction was maintained at the desired temperature under vigorous stirring. To track the reaction progress, the reaction was stopped at a certain time interval and the mixture was collected with a syringe. The filtrate was extracted by $CH_3COOC_2H_5$ followed by filtrating through a 0.45 μm membrane filter. The reaction conversion of the HDC of CPs was evaluated by GC. The Pd/NMC catalyst was recovered by centrifugation and then washed with water and dried in vacuum at room temperature for the next catalytic cycle to investigate the reusability. For comparison, commercial Pd/AC catalyst was utilized in HDC of CPs.

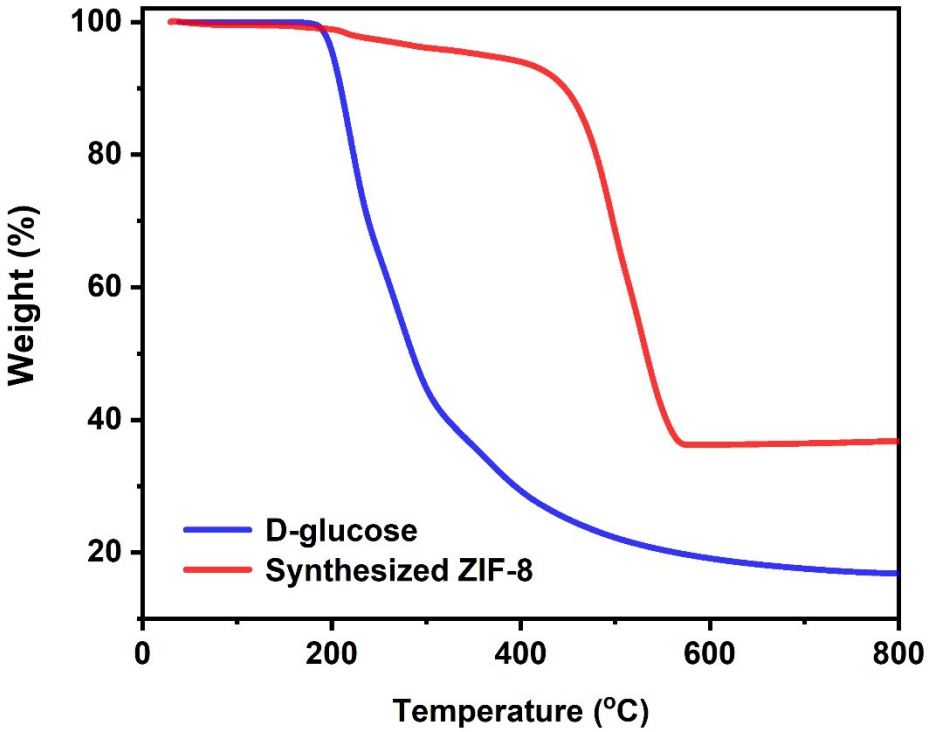

Figure S1 TGA analyses of synthesized ZIF-8 and D-glucose.

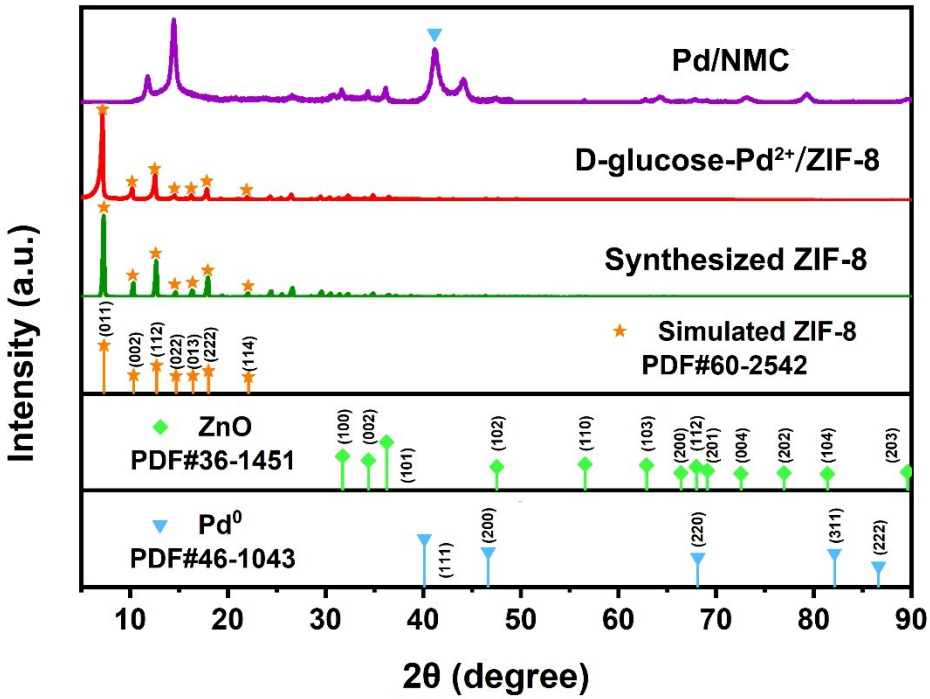

Figure S2 XRD patterns of Pd^0 (PDF#46-1043), ZnO (PDF#36-1451), simulated ZIF-8 (PDF#60-2542), synthesized ZIF-8, D-glucose-Pd^{2+}/ZIF-8 and Pd/NMC.

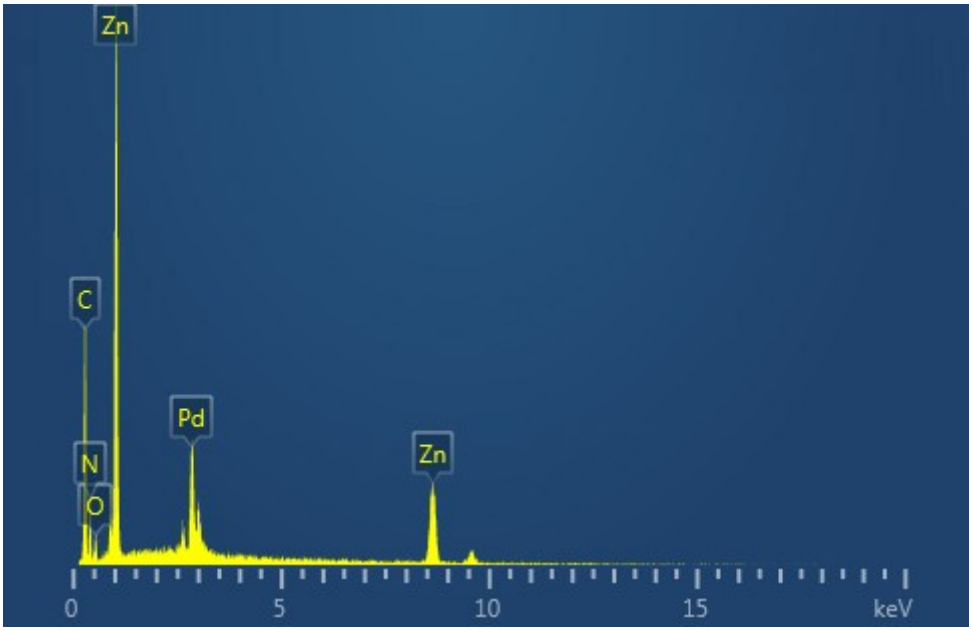

Figure S3 Element analysis of Pd/NMC.

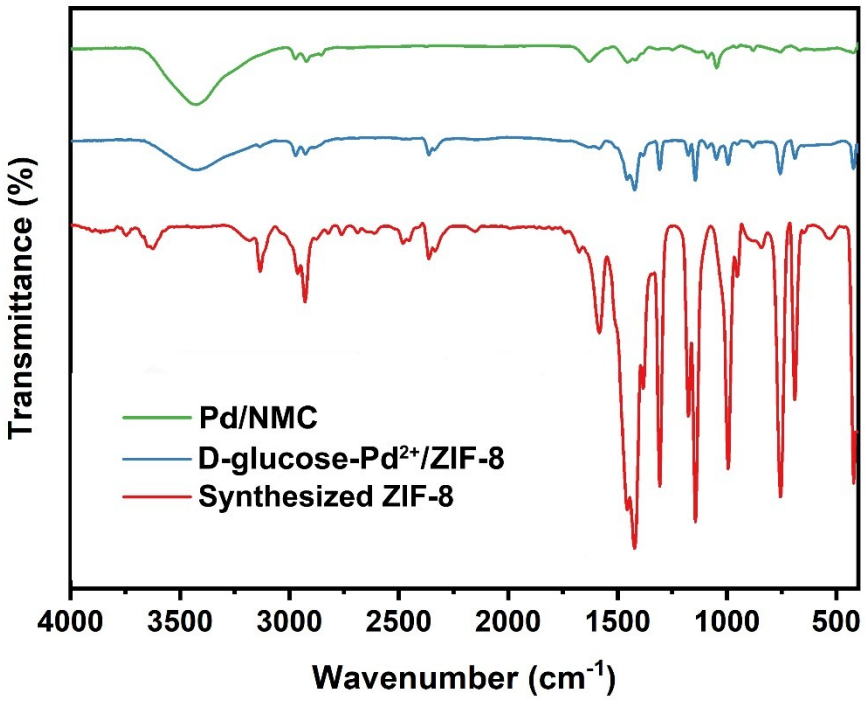

Figure S4 FT-IR spectra of synthesized ZIF-8, D-glucose-Pd^{2+}/ZIF-8 and Pd/NMC.

In the FT-IR spectrum of ZIF-8 (Figure S4), the peaks at 3,133 cm^{-1} and 2,929 cm^{-1} are attributed to the stretching vibrations of C-H bonds, respectively.[2] The peak at 1,580 cm^{-1} can be assigned as the C=N stretch mode of ZIF-8, and the peaks in the range of 650-1,500 cm^{-1} are associated with the nitrogen heterocyclic ring stretching or bending.[3] In the spectrum of D-glucose-Pd^{2+}/ZIF-8, almost all of the peaks are in good agreement with those of ZIF-8, except the peak at 3,450 cm^{-1} that is attributed to the stretching vibrations of -OH in the D-glucose.[4] The spectrum of Pd/NMC shows identical peaks with ZIF-8 and D-glucose-Pd^{2+}/ZIF-8 in the range of 650-1,500 cm^{-1}, while the intensity of these peaks is substantially lower than those of ZIF-8 and D-glucose-Pd^{2+}/ZIF-8. The peak at 3,450 cm^{-1} is related to -OH maintained in the Pd/NMC.

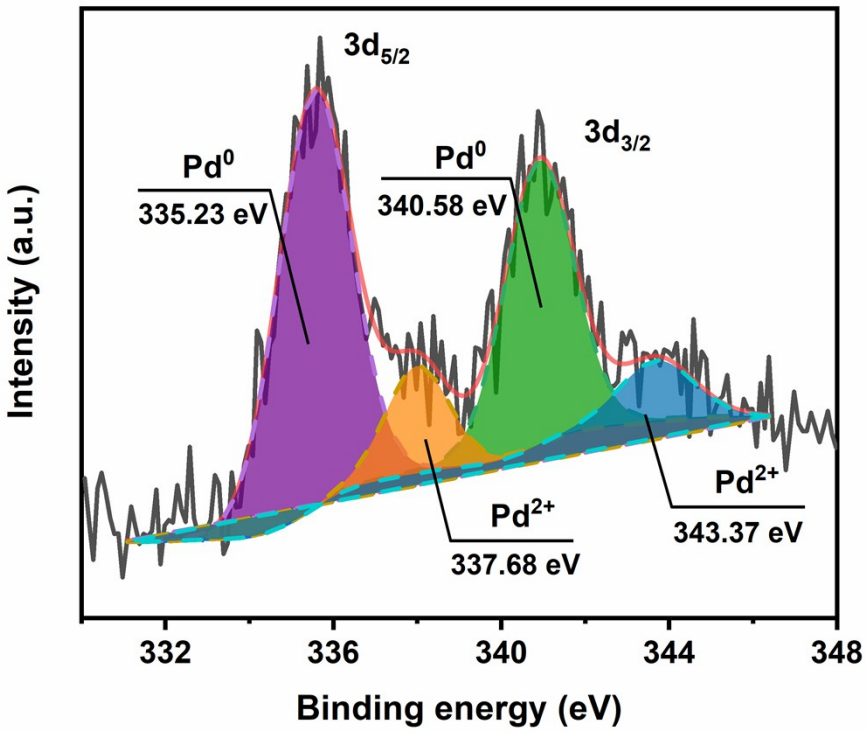

Figure S5 Pd 3d XPS spectrum of Pd/NMC.

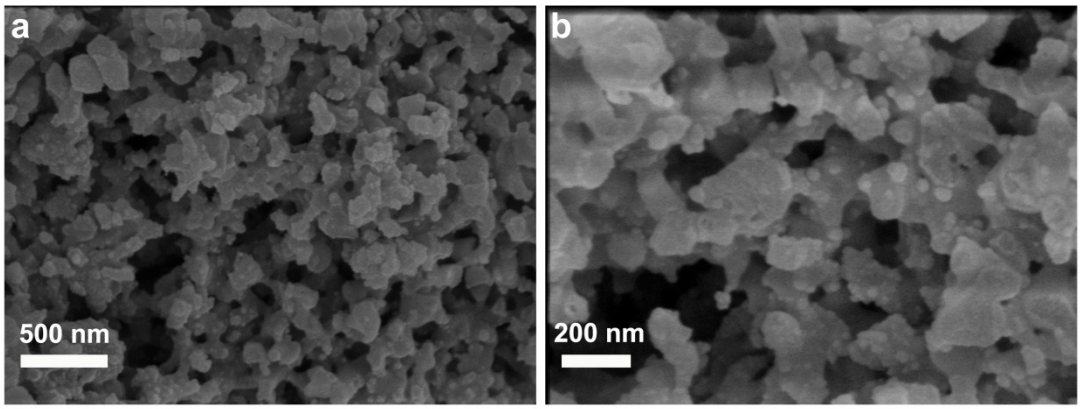

Figure S6 SEM images of Pd/NMC after 6 cycles.

Table S1. Catalytic hydrodechlorination performances of different catalysts

Catalyst	Base	Time (min)	Conversion (%)
Pd/NMC	none	80	54.6
None	NaOH	80	-
NMC	NaOH	80	-
Pd/AC	NaOH	80	79.3

Reaction conditions: NaOH (1.5 mmol), 4-CP (1.5 mmol), H_2O 30 mL, catalyst 15 mg, H_2 balloon, and 30 ^oC.

References

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4. T. Zhang, L. Lin, X. Zhang, H. Liu, X. Yan, Z. Liu and K. L. Yeung, Appl. Surf. Sci., 2015, **351**, 1184-1190.