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Defective Pt nanoparticles encapsulated in mesoporous metal-organic framework for enhanced catalysis

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1. Materials and Instrumentation.

The reagents chromium(III) nitrate nonahydrate ($Cr(NO_3)_3\cdot9H_2O$), 1,4-benzene dicarboxylic acid, aqueous HF, $H_2PtCl_6\cdot6H_2O$, $CoCl_2$,·anhydrous *n*-hexane, nitrobenzene, 4-chloronitrobenzene, 4-nitrotoluene, 4-Nitrobenzaldehyde, 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, acetone, ethanol, and N,N-dimethylformamide (DMF) were purchased from Tansoole, deionized water with the specific resistance of 18.25 MΩ·cm. Other reagents and solvents were obtained from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) patterns were performed on a Miniflex 600 diffractometer using Cu-Ka radiation (λ = 0.154 nm, 30 kV, 15 mA). Nitrogen sorption isotherms were measured by a Micromeritics ASAP 2020 system at desired temperature, prior to nitrogen adsorption/desorption measurement, the samples were dried for 12 h at 393 K under vacuum. The size and morphologies of catalysts were studied using a FEIT 20 transmission electron microscope (TEM) and HRTEM working at 200 kV. Valence state of element was measured by X-ray photoelectron spectroscopy (XPS) on an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher) using an Al Ka source (15 kV, 10 mA) with Ar etching for 30 min. The contents of Pt and Co in catalyst were quantified by inductively coupled plasma atomic emission spectroscopy

(ICP-AES) on an Ultima 2 analyzer (Jobin Yvon). The catalytic reaction products were analyzed and identified by gas chromatography-mass spectrometer (Agilent, 7890B).

2. Catalyst Preparation.

Preparation of MIL-101: MIL-101 was synthesized and purified according to the reported procedures.[S1] Typically, $Cr(NO_3)_3·9H_2O$ (4.33 g, 10 mmol), 1,4-benzene dicarboxylic acid (1.8 g, 10 mmol), de-ionized water (70 mL) and aqueous HF (0.5 mL, 2.5 mmol) were introduced into a Teflon-lined autoclave and heated at 220 °C for 8 h in an oven under static condition. After the reaction mixture was cooled down to room temperature, crystals were purified using the boiling water for 24 h to remove organic species trapped within the pores, after filtering with the glass filter, the resulting solid was purified twice in ethanol at reflux temperature for 24 h, then the crystalline MIL-101 product was further purified by solvothermal treatment in hot ethanol at 100 ºC for 24 h. To obtain the pure crystals, the as-synthesized MIL-101 was further activated by the aqueous NH_4F solutions. The sample was finally dried at 150 °C for 12 h under in vacuum for further use.

Preparation of Pt_mCo_n@MIL-101: Encapsulation of Pt^{4+} and Co^{2+} precursors were carried on MIL-101 by double solvent method.[S2] Typically, 130 mg MIL-101 sample, which was pre-activated at 150 °C for 5 h, was added into 20 mL of dry n-hexane as hydrophobic solvent and sonicated for 30 min until the mixture dispersed uniformly. Then 90 μL of $H_2PtCl_6·6H_2O$ and $CoCl_2$ mixed precursors solution with various concentration as the hydrophilic solvent was dropwise added to the above suspension within 30 min under continuously vigorous stirred. After stirring for 5 h and removed n-hexane, the obtained $Pt^{4+}Co^{2+}$@MIL-101 was suspended in 20 ml water and reduced by prepared 2 M aqueous $NaBH_4$ solution for 5 h, then washed with acetone twice and dried in vacuum at 70 °C for further use. The corresponding Pt and Co content was determined by ICP. **Table S1**

Preparation of Pt(Co)@MIL-101: PtCo@MIL-101 was re-dispersed into 3.4 vol% HNO_3 under stirring for 5 h. Pt(Co)@MIL-101 was obtained by washing with acetone, then centrifugation and dried at 120 °C for 12 h under vacuum for further use. The corresponding Pt and Co content was determined by ICP. **Table S1**

Table S1 Different atomic ratio of Pt:Co in PtCo@MIL-101 and the corresponding catalyst Pt(Co)@MIL-101 based on ICP-AES.

Pt_mCo_n@MIL-101	Pt(wt%)	Co(wt%)
Pt@MIL-101	1.2	-
Co@MIL-101	-	1.09
Pt_5Co_4@MIL-101	1.04	0.239
Pt_5Co_{16}@MIL-101	1.06	1.09
Pt_5Co_{64}@MIL-101	1.13	4.01
$Pt_5(Co)_4$@MIL-101	0.9	0.0183
$Pt_5(Co)_{16}$@MIL-101	0.56	0.0153
$Pt_5(Co)_{64}$@MIL-101	0.59	0.0147

3. Catalytic Performance.

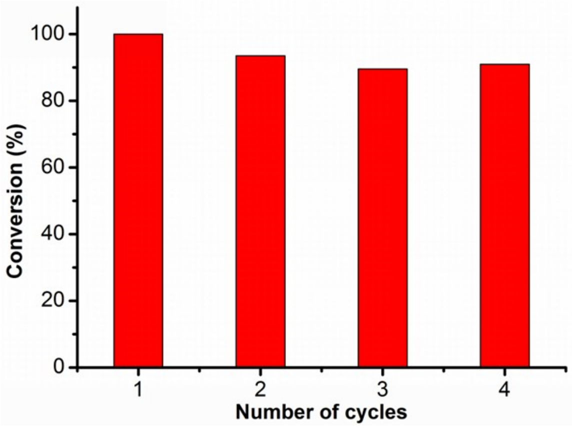
Catalytic performance evaluation for PtCo@MIL-101 in hydrogenation of nitroarenes reaction: In a typical procedure, catalyst (containing 0.1 mmol PtCo) was dispersed in 5 mL ethanol, and then a certain amount of substrate(0.2 mmol) was added. The reactor was sealed, purged with hydrogen and pressurized to 0.1 MPa, followed by stirring with a magnetic stirrer at a rate of 300 rpm at 35 ℃. After reaction, the mixturewas separated by centrifugation. The reactants were analyzed by GC (Agilent 7890A), and all products were confirmed by GC-MS (Agilent 7890B).

Table S2 Catalytic performance comparison between Pt(Co)@MIL-101 and previously reported Pt-M based catalysts toward the nitrobenzene hydrogenation.

Catalyst	**Reaction condition**	**TOF (h^{-1})** **（Selectivity）**	**References in paper**
Pt@MIL-101	Ethanol, 25℃, 4 MPa H_2	18053 (-)	S3
Pt@MIL-101	Ethanol, 20℃, 1 MPa H_2	7074 （91.6%）	S4
Pt_8Co_1@UiO-66	Isopropyl alcohol 25℃, 1 atm H_2	200 （100%）	S5
Pt@UiO-66	Hexane, 25℃,2 atm H_2	322 (72.5%)	S6
$Pt_5(Co)_{64}$@MIL-101	Ethanol, 35℃, 1 atm H_2	496 （100%）	This work

Table S3 Catalytic recyclability of $Pt_5(Co)_{64}$@MIL-101 for nitrobenzene hydrogenation.

Run	**Yield(%)**	**Selectivity**
1	**100**	**100**
2	**93.5**	**93.5**
3	**89.6**	**89.6**
4	**91**	**91**



Reaction conditions: 0.2 mmol nitrobenzene, 5 mg $Pt_5(Co)_{64}$@MIL-101, 5 mL EtOH, 35℃; the yield was evaluated at 1h for each run.

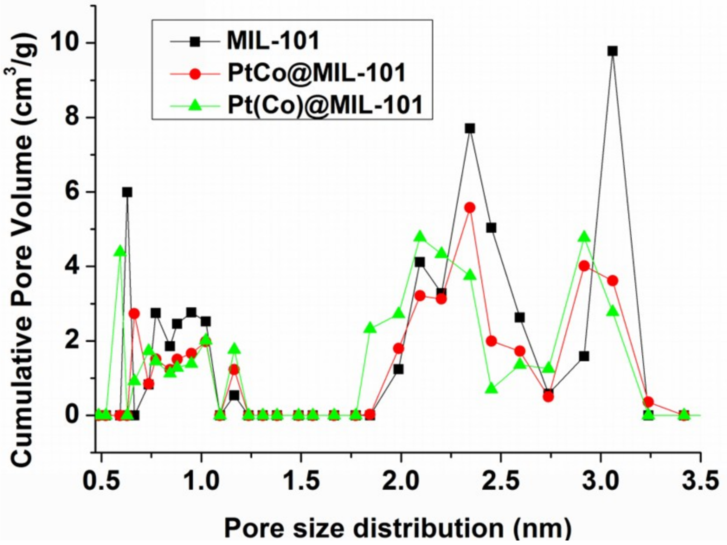


Fig. S1 Pore size distribution of MIL-101, PtCo@MIL-101 and Pt(Co)@MIL-101.

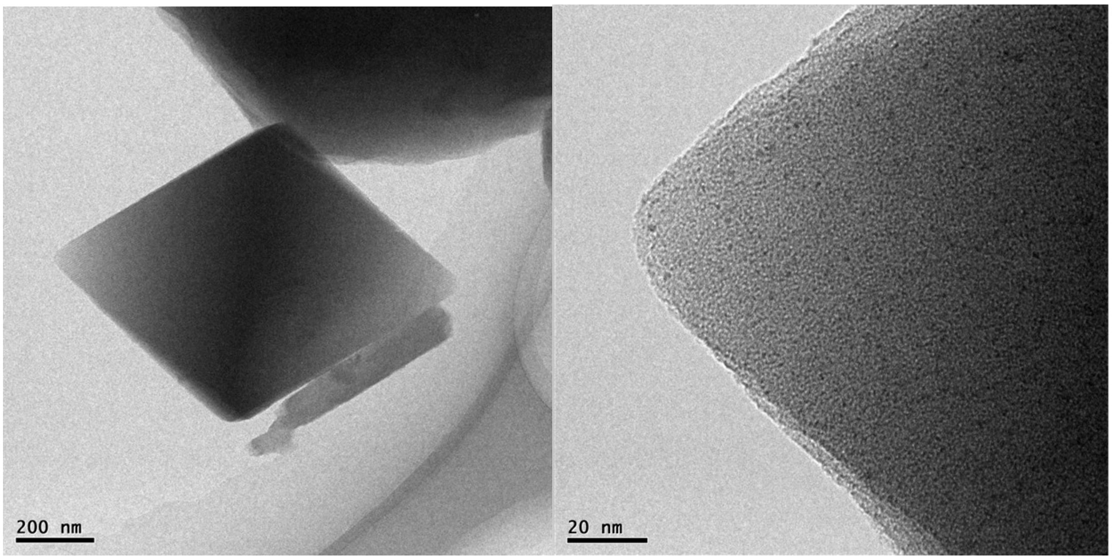


Fig. S2 TEM image of Pt_5Co_{16}@MIL-101.

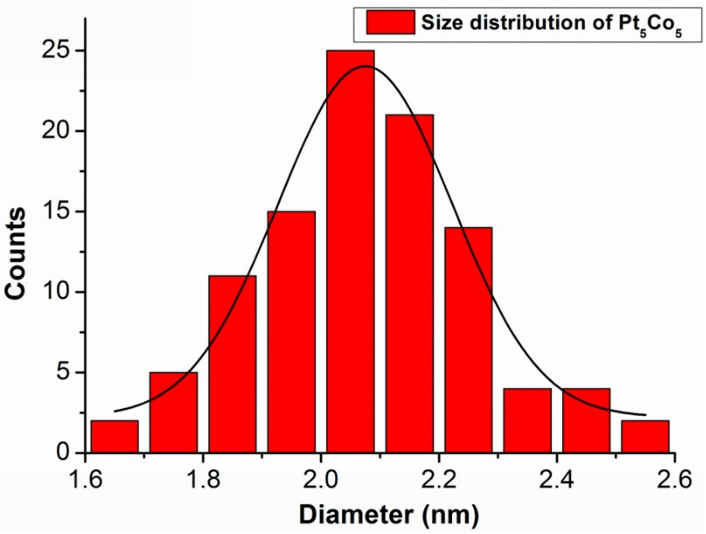


Fig. S3 Pt_5Co_{16} NPs size distribution of Pt_5Co_{16}@MIL-101.

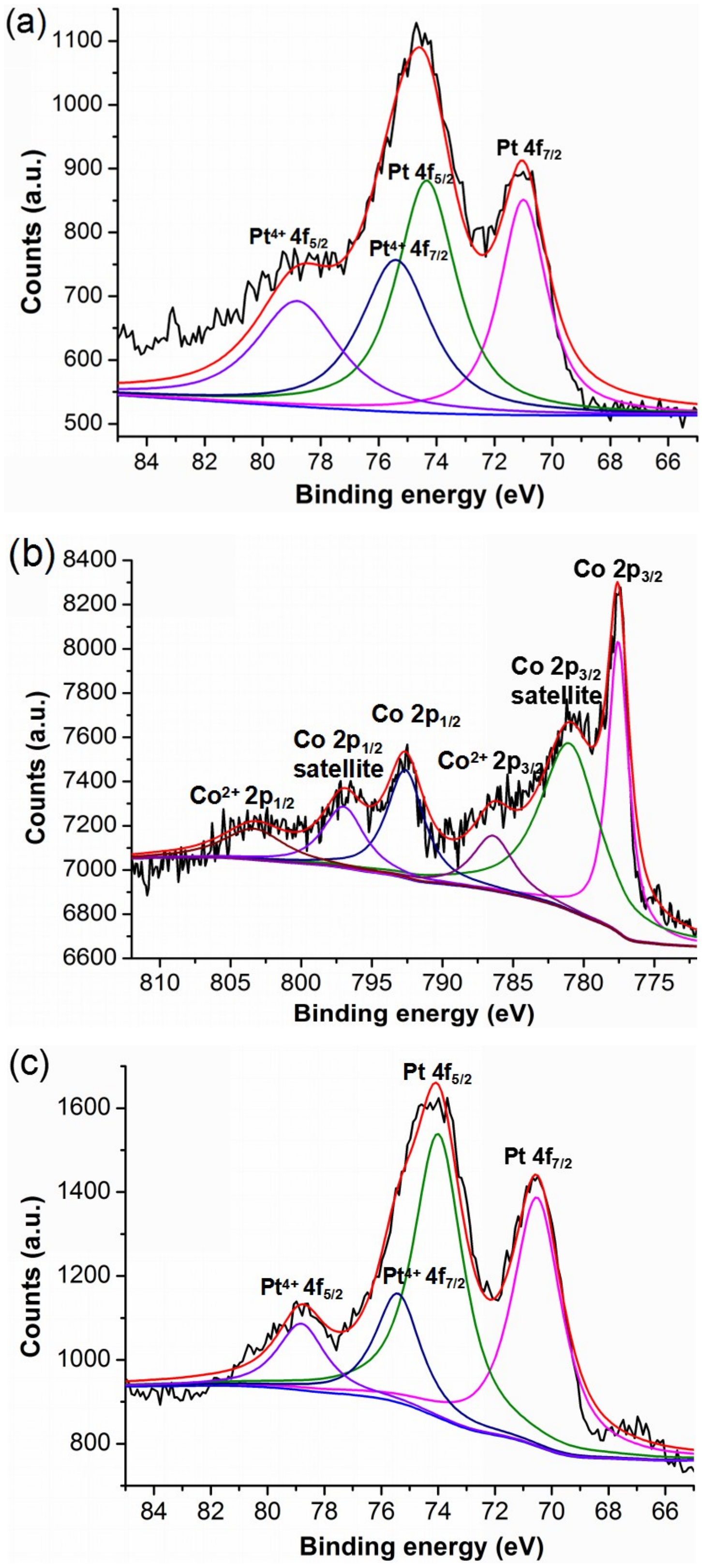


Fig. S4 (a) Pt 4f XPS spectra of Pt_5Co_{16}@MIL-101; (b) Co 2p XPS spectra of Pt_5Co_{16}@MIL-101; (c) Pt 4f XPS spectra of $Pt_5(Co)_{16}$@MIL-101.

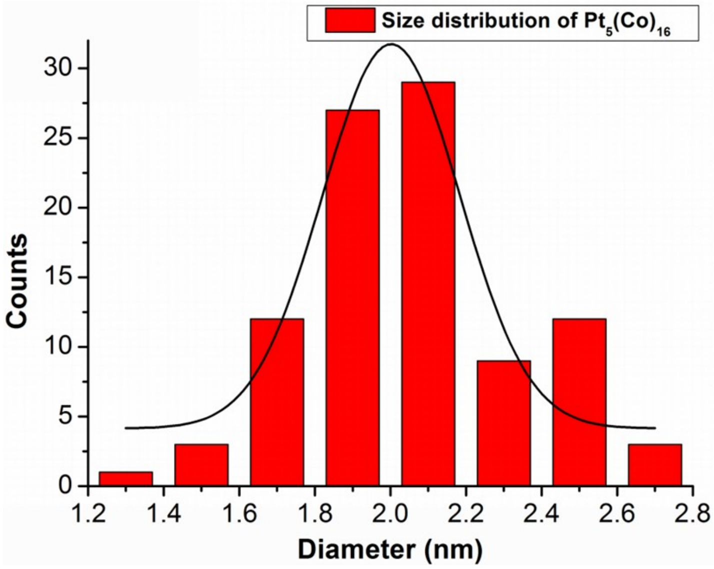


Fig. S5 $Pt_5(Co)_{16}$ NPs size distribution of $Pt_5(Co)_{16}$@MIL-101.

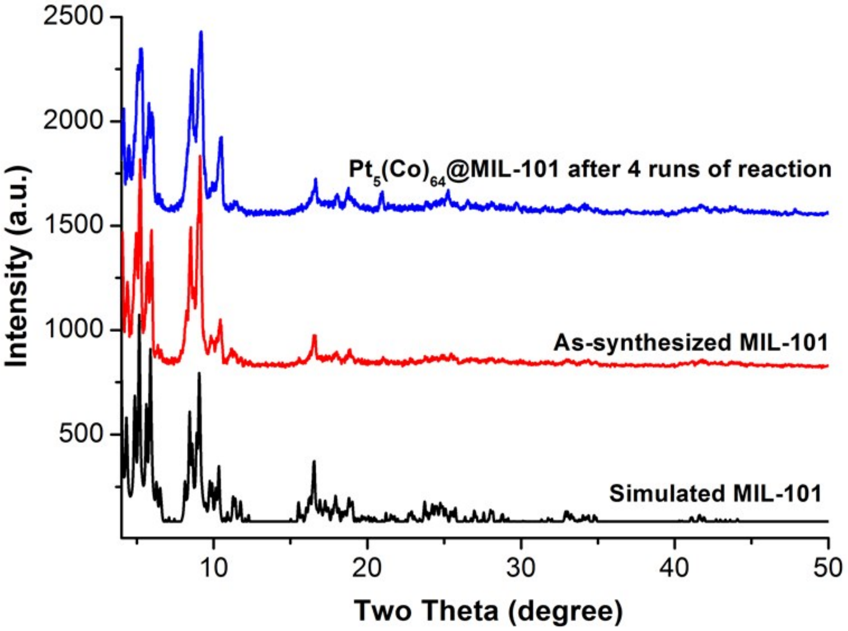


Fig. S6 Powder XRD patterns of simulated MIL-101, as-synthesized MIL-101 and $Pt_5(Co)_{16}$@MIL-101 after 4 cycles of hydrogenation of nitrobenzene.

References

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