Supporting Information

One-Pot Synthesis of Pd@MOF Composites without the Addition of Stabilizing Agents

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Materials and Methods

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Experimental

1. Catalysts preparation

All chemicals were purchased from commercial sources and used without further treatments.

1.1 One-pot synthesis of Pd@MOF1

For the synthesis of 2.0% Pd@MOF1: ZrCl₄ (67 mg), H₂bpydc (2,2'-bipyridine-5,5'dicarboxylic acid) (90 mg), concentrated HCl (0.5 mL) and 5.8 mg Pd(NO₃)₂ were dispersed in DMF (13 mL) in a 25 mL tube. The slurry was subjected to ultrasounication (180 Watt) for 20 min and was then magnetically agitated at room temperature. An appropriate amount of NH₃BH₃ was dissolved in 2 mL DMF and added to the above suspension under vigorous agitation. Then the sample was sealed and heated at 80 °C for 20 hours. The produced powders were isolated by centrifugation, washed first with DMF (2 x 30 mL) and then with chloroform (2 x 20 mL). The sample was slowly dried in air at room temperature for 1 h, further dried under vacuum at 150 °C overnight to remove the solvents. Different Pd contents could be loaded by adding different amount of Pd precursor to the starting materials for the MOF composite.

1.2 One-pot synthesis of Pd@MOF2

An identical protocol was applied for the preparation of Pd@MOF2 catalysts except for the use of H_2 bpdc (*para*-biphenyldicarboxylic acid) as ligand instead of H_2 bpydc.

1.3 Synthesis of MOF1

 $ZrCl_4$ (67 mg), bpydc (90 mg), concentrated HCl (0.5 mL) were dispersed in DMF (15 mL) and sealed in a 25 mL tube at 80 °C for 20 hours. The produced powders were isolated by centrifugation, washed first with DMF (2 x 30 mL) and then with chloroform (2 x 20 mL).

The sample was slowly dried in air at room temperature for 1 h, further dried under vacuum at 150 °C overnight to remove the solvents.

1.4 One-pot synthesis of Au@MOF1

For the synthesis of Au@MOF1, identical procedures were followed to synthesize Au@MOF1 as for the synthesis of Pd@MOF1 except for the use of $HAuCl_4$ ·4H₂O as metal precursor.

1.5 One-pot synthesis of Pt@MOF1

An identical protocol was applied for the preparation of Pt@MOF1 catalysts except for the use of $H_2PtCl_6·6H_2O$ as metal precursor.

2. Catalyst characterization and catalytic reactions

2.1 Characterization

The BET surface area measurements were performed with N_2 adsorption isotherms at 77 K on a Micromeritics ASAP 2020M instrument. Before the analysis, the samples were evacuated at 150 °C for 12 h.

Powder X-ray diffraction patterns of the samples were recorded on a Rigaku diffractormeter (D/MAX-IIIA, 3 kW) using Cu K α radiation (40 kV, 30 mA, λ = 0.1543 nm). The size and morphology of Pd@MOF composites were investigated by using a transmission electron microscope (TEM, JEOL, JEM-2010HR) with EDX analysis (Oxford INCA EDS) operated at 300 kV. The palladium contents of the samples were determined quantitatively by AAS on a HITACHI Z-2300 instrument.

2.2 Catalytic reactions

Typical procedures for hydrogenation of cinnamaldehyde: cinnamaldehyde (0.1 mmol) and supported palladium catalyst (1 mol%) were added to 2 mL of THF. The reaction mixture

was stirred at room temperature under 1 atm hydrogen atmosphere for 6 h. Upon reaction completion, the catalyst particles were removed from the solution by filtration and washed with THF. The liquid phase was subsequently analyzed by GC/MS (Shimadzu GCMS-QP5050A equipped with a 0.25 mm \times 30 m DB-WAX capillary column).

For the recyclability tests, the reactions were performed under the same reaction conditions as described above, except using the recovered catalyst. Each time, the catalyst was isolated from the reaction solution at the end of the reaction, washed with toluene, and then heated at 150 °C under vacuum.



Figure S1. TEM image of 2.0% Pd@MOF1-80.



Figure S2. XPS spectra of the Pd 3d and Zr 3p regions for 2.0% Pd@MOF1.



Figure S3. Powder XRD patterns of Pd@MOF composites: (a) simulated MOF1; (b) MOF1; (c) 0.5% Pd@MOF1; (d) 1.0% Pd@MOF1; (e) 2.0% Pd@MOF1; (f) 4.0% Pd@MOF1; (g) 2.0% Pd@MOF2; (h) 2.0% Pd@MOF1 after five runs.



Figure S4. X-ray crystal structure of MOF1.



Figure S5. Nitrogen adsorption isotherms at 77 K of MOF1 (♠), 0.5% Pd@MOF1 (■), 1.0% Pd@MOF1 (▲), 2.0% Pd@MOF1 (×), 2.0% Pd@MOF2 (○), 4.0% Pd@MOF1 (●).



Figure S6. TGA curve of 2.0% Pd@MOF1.



Figure S7. TEM images of (a) 1.0% Au@MOF1 and (b) 1.0% Pt@MOF1.

Table S1. Condition modification for the synthesis of Pd@MOF1^a and their catalytic performance.^b

Pd precursor

	$\operatorname{ZrCl}_4 + \sum_{O}^{HO} \overline{\langle N \rangle}_N$	N OH Reducing ag	$ \stackrel{\text{or}}{\blacktriangleright} Pd@MOF1 \\ \stackrel{\text{ent}}{\longrightarrow} Pd@MOF1 $	
		$0 \xrightarrow{H_2(1atm) r.t.}$	\searrow_0	
Sample	Pd precursor	Reducing agent	Amount	Yield (%) ^c
1	$PdCl_2(CH_3CN)_2$	EtOH	0.5 ml	
2	$PdCl_2(CH_3CN)_2$	EtOH	1.0 ml	
3	$PdCl_2(CH_3CN)_2$	EtOH	2.0 ml	
4	$PdCl_2(CH_3CN)_2$	MeOH	0.5 ml	
5	$PdCl_2(CH_3CN)_2$	MeOH	1.0 ml	
6	$PdCl_2(CH_3CN)_2$	Glycol	1.0 ml	
7	$PdCl_2(CH_3CN)_2$	Glycol	2.0 ml	
8	$PdCl_2(CH_3CN)_2$	NaBH ₄	0.01 M	
9	$PdCl_2(CH_3CN)_2$	Vitamin C	0.01 M	
10	PdCl ₂ (CH ₃ CN) ₂	Sodium citrate	0.01 M	30
11	$PdCl_2(CH_3CN)_2$	NH ₃ BH ₃	40 mg	51
12	$Pd(NO_3)_2$	NH ₃ BH ₃	40 mg	100

^a Catalysts preparation condition: 67 mg ZrCl₄, 90 mg H₂bpydc, 0.45 ml HCl, 2.0 wt% Pd to the starting materials to prepare the MOFs, 10 ml DMF. ^b The prepared catalysts were applied in the hydrogenation of cinnamaldehyde. Reaction condition: cinnamaldehyde (0.1 mmol), catalyst (Pd 1 mol%), THF (2 ml), 1 atm H₂, 25 °C, 6 h. ^c The yield of HCAL was determined by GC-MS analysis.

Sample	$S_{BET}\left(m^2~g^{-1}\right)$	$S_{Langmuir}(m^2~g^{-1})$	$V_{pore} (cm^3 g^{-1})$
MOF1	2470	3146	1.11
0.5% Pd@MOF1	2044	2631	0.93
1.0% Pd@MOF1	1808	2331	0.81
2.0% Pd@MOF1	1571	2006	0.71
4.0% Pd@MOF1	1304	1695	0.58
2.0% Pd@MOF 2	1572	1983	0.70

 Table S2. Surface areas and pore volumes of the Pd@MOF composites.

Entry	Subtrate	Product	Time (h)	Yield (%) ^b
1			7	99
2	Meo	MeO	7	>99
3	CI CI	CI CI	5	>99
4		OMe	10	98

Table S3. Hydrogenation of various cinnamaldehydes catalyzed by 2.0% Pd@MOF1.^a

^{*a*} Reaction condition: cinnamaldehyde (0.1 mmol), 2.0% Pd@MOF1 (Pd 1 mol%), THF (2 ml), 1 atm H₂, 25 °C. ^{*b*} The yield was determined by GC-MS analysis.

Entry	Catalyst	Conversion	Selectivity (%)		
		(%)	HCAL	HCOL	COL
1	1.0% Au@MOF1	72	4	8	88
2	1.0% Pt@MOF1	100	83	2	15

Table S4. Results of hydrogenation of cinnamaldehyde (CAL).^a

^{*a*} Reaction condition: cinnamaldehyde (0.1 mmol), substrate/metal = 100, THF (2 mL), 1 atm H_2 , 25 °C. ^{*b*} The conversion and selectivity were determined by GC-MS analysis.