

Multifunctional Catalysis by Pd@MIL-101: One-Step Synthesis of Methyl Isobutyl Ketone over Palladium Nanoparticles Deposited to Metal-Organic Framework

Yingyi Pan, Bizhen Yuan, Yingwei Li* and Dehua He*

Experimental

1. Synthesis of Pd@MIL-101

MIL-101 was prepared from hydrothermal reaction of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.80 g, 2 mmol), HF (48 wt %, 2 mmol), terephthalic acid (0.33 g, 2 mmol), and 10 mL deionized water at 220 °C for 8 h.^[1] The mixture was cooled first to 150 °C in 1 h, and then slowly to room temperature in 12 h. Upon the slow cooling procedure, most of the residual carboxylic acid was in large crystals that can be easily isolated from the solution and MIL-101 powder by using a large pore fritted glass filter (n°2, Schott). The free terephthalic acid was eliminated and the green MIL-101 powder was isolated from the solution using a small pore paper filter (1°, Whatman). The powder was washed thoroughly with deionized water and ethanol, and then soaked in ethanol (95 % EtOH with 5 % water) at 80 °C for 24 h. The solid was finally dried overnight at 150 °C under vacuum.

Supported palladium was prepared via incipient wetness impregnation of MIL-101 with desired quantitative $\text{Pd}(\text{NO}_3)_2$ diluted in DMF at room temperature. The as-synthesized sample was slowly dried in air at room temperature for 24 h, and then treated in a stream of H_2 at 200 °C for 2 h to yield Pd@MIL-101. The Pd loading on the sample was 0.05, 0.11, 0.22, 0.34, 0.87, and 2.79 wt%, respectively, based on Atomic Absorption Spectroscopy (AAS) analysis.

2. Characterization

Powder X-ray diffraction patterns of the MIL-101 and Pd@MIL-101 samples were obtained by a Rigaku diffractometer (D/MAX-III A, 3 kW) using $\text{Cu K}\alpha$ radiation (40 kV, 30 mA, $\lambda = 0.1543$ nm). The BET surface area measurements were performed with N_2 adsorption/desorption isotherms at 77 K on a Micromeritics ASAP 2010 instrument. Before the analysis, the samples were evacuated at 150 °C for 12 h. The size and morphology of Pd@MIL-101 were investigated by using a transmission electron microscope (TEM, JEOL, JEM-2010HR) with EDX analysis (Oxford INCA EDS) at 300 kV. Thermogravimetric analysis (TGA) of samples was performed on a NETZSCH STA449C instrument using a constant heating rate of 10

$^{\circ}\text{C min}^{-1}$ under N_2 atmosphere. The palladium contents of the samples were determined quantitatively by atomic absorption spectroscopy (AAS) on a HITACHI Z-2300 instrument.

Acid-base properties were determined by NH_3 -, and CO_2 -TPD measured by the pulse technique using a Micromeritics AutoChem II 2920 instrument using TCD detection. Typically, a sample of 100 mg was pretreated under a flow of helium (50 ml min^{-1}) at $150 \text{ }^{\circ}\text{C}$ for 3 h. Then the temperature was lowered to $100 \text{ }^{\circ}\text{C}$ under a flow of He. The analysis was performed by successive pulse of 1 ml of ammonia (or CO_2) into the He flow using a loop. The TPD data were collected from $100 \text{ }^{\circ}\text{C}$ to $400 \text{ }^{\circ}\text{C}$ at a heating rate of $10 \text{ }^{\circ}\text{C min}^{-1}$ in a helium flow.

Pd dispersion in the catalysts was determined by CO chemisorption measured by the pulse technique using a Micromeritics AutoChem II 2920 apparatus. Before analysis, the sample was treated at $200 \text{ }^{\circ}\text{C}$ in H_2 for 1 h. The dispersion, D , defined as the fraction of palladium at the surface, $D = \text{Pd}_s/\text{Pd}_{\text{total}}$, was calculated with the assumption of one CO molecule per surface Pd.^[2]

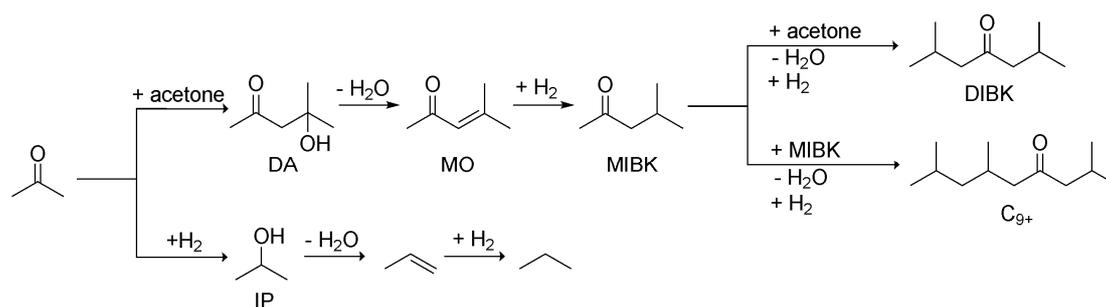
3. Catalytic measurements

The liquid-phase synthesis of MIBK was performed in a 60 ml Teflon-lined stainless steel autoclave equipped with a pressure gauge and a magnetic stirrer. Typically, 2.0 g of acetone, 0.2 g of catalyst, and 0.3 g of decane (internal GC standard) were added to the autoclave and the mixture was stirred at a constant stirring speed of 800 rpm. The reaction time was 1.5 h unless stated otherwise. The autoclave was purged five times with H_2 , then pressurized with H_2 and loaded in an oil bath, which was preheated to the target temperature. Most of the acetone remained liquid under such conditions during the reactions, as judging from the resulting pressure at each reaction temperature. At the end of the reaction, the autoclave was cooled to $0 \text{ }^{\circ}\text{C}$ by placing it to an ice bath. The gaseous products were collected with a gas bag. The reaction products were identified with a GC-MS (Shimadzu QP5050A) and analyzed by a GC (Agilent 6820) equipped with a flame ionization detector and a $0.25 \text{ mm} \times 30 \text{ m}$ capillary column (DB-WAX).

For the recyclability test, the catalyst was isolated from the reaction solution at the end of each catalytic reaction, washed with acetone, and then dried at $150 \text{ }^{\circ}\text{C}$ under vacuum. The dried catalyst was then reused in the second run. The catalytic activity and MIBK selectivity of the catalyst was also obtained in the second run, showing that the framework of the catalyst may remain intact during the catalytic cycles. The catalyst remained effective for up to 5 cycles for the reaction (Table S4).

Reference

- [1] Y. K. Hwang, D. Y. Hong, J. S. Chang, S. H. Jung, Y. K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre, G. Ferey, *Angew. Chem. Int. Ed. Engl.* **2008**, *47*, 4144.
- [2] G. Agostini, R. Pellegrini, G. Leofanti, L. Bertinetti, S. Bertarione, E. Groppo, A. Zecchina, C. Lamberti, *J. Phys. Chem. C* **2009**, *113*, 10485.



Scheme S1: Main reactions during acetone transformation reaction.

Table S1: Characterization results of Pd@MIL-101 catalysts.

Pd loading [wt%]	S_{BET} [$\text{m}^2 \text{g}^{-1}$]	Pore volume [$\text{cm}^3 \text{g}^{-1}$]	Pd dispersion [D] ^[a]	Pd_s [wt%] ^[b]	Acid site density [mmol g^{-1}]
-	3115	1.58	-	-	2.91
0.11	2959	1.49	0.58	0.06	2.88
0.22	2793	1.42	0.40	0.09	2.60
0.34	2627	1.35	0.26	0.09	2.16
0.87	2656	1.36	0.15	0.13	1.68
2.79	2731	1.40	0.05	0.14	1.15

[a] Determined by CO chemisorption. [b] Accessible surface Pd. $\text{Pd}_s = D \times \text{Pd}_{\text{total}}$.

Table S2: Effect of reaction temperature on the liquid-phase synthesis of MIBK over 0.11 wt% Pd@MIL-101 catalyst.^[a]

Temperature [°C]	Conv. [%]	Selectivity [%] ^[b]					
		MIBK	DIBK	C ₃	IP	MO	Others
120	26.6	80.5	1.0	0.5	15.7	1.5	0.8
135	46.2	91.6	3.2	0.6	1.2	2.0	1.2
150	59.8	90.2	5.8	0.8	0.2	0.7	2.3
165	66.6	77.6	10.8	1.2	4.9	1.6	4.0
180	73.5	65.5	15.8	1.5	6.6	1.7	8.5

[a] Reaction conditions: 0.75 MPa H₂ pressure (RT), 2.0 g acetone, 0.2 g catalyst, 800 rpm stirring speed, 1.5 h, 60 ml autoclave. [b] As in Table 1.

Table S3: Liquid-phase synthesis of MIBK over various Pd catalysts.^[a]

Catalyst	Conv. [%]	Selectivity [%] ^[b]					
		MIBK	DIBK	C ₃	IP	MO	Others
0.12% Pd/Zn:Cr (1:1) ^[c]	28.9	86.6	6.3	1.0	0.3	0.8	4.9
0.10% Pd/MCM-22 ^[d]	25.6	88.5	5.0	1.3	0.9	0.5	3.8
0.11% Pd@MIL-101	59.8	90.2	5.8	0.8	0.2	0.7	2.3

[a] Reaction conditions: 150 °C, 0.75 MPa H₂ pressure (RT), 2.0 g acetone, 0.2 g catalyst, 800 rpm stirring speed, 1.5 h, 60 ml autoclave. [b] As in Table 1. [c] Pd supported Zn-Cr mixed oxide was prepared following the procedure described in ref. 8(e). [d] Prepared following the procedure described in the reference as below: P. Yang, Y. Shang, J. Yu, J. Wang, M. Zhang, T. Wu, *J. Mol. Catal. A: Chem.*, 2007, **272**, 75.

Table S4: Recycling studies over 0.11 wt% Pd@MIL-101 catalyst.^[a]

Run	Conv. [%]	Selectivity [%] ^[b]					
		MIBK	DIBK	C ₃	IP	MO	Others
1	59.8	90.2	5.8	0.8	0.2	0.7	2.3
2	58.4	91.2	4.6	0.7	0.2	0.5	2.6
3	60.5	89.8	6.3	1.0	0.4	0.7	2.1
4	59.0	90.6	5.2	0.6	0.3	0.6	2.5
5	61.1	89.0	6.2	0.9	0.3	0.5	2.8

[a] Reaction conditions: 150 °C, 0.75 MPa H₂ pressure (RT), 2.0 g acetone, 0.2 g catalyst, 800 rpm stirring speed, 1.5 h, 60 ml autoclave. [b] As in Table 1.

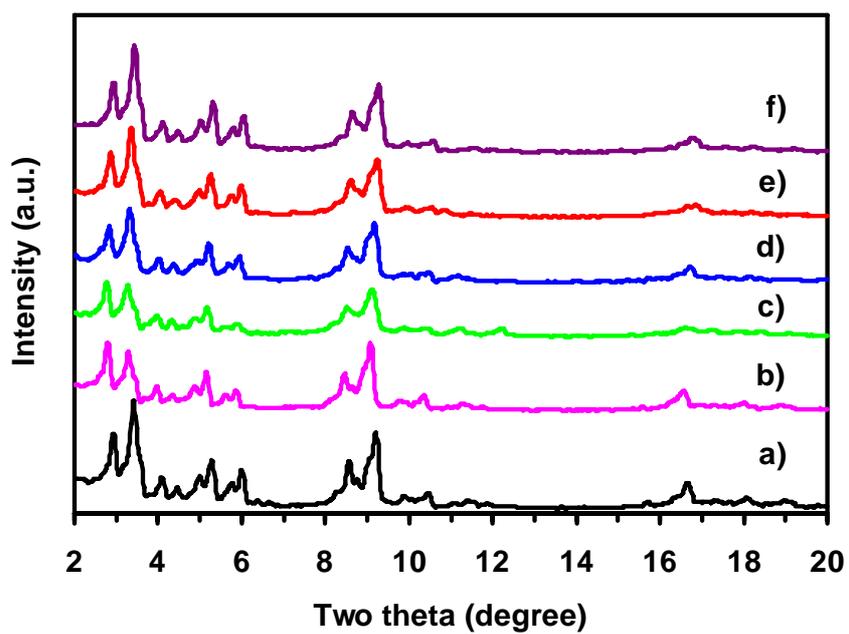


Fig. S1 XRD patterns of MIL-101 samples. Sample a) is the as-synthesized MIL-101, and samples b)-f) are Pd@MIL-101 with Pd loading of 0.11, 0.22, 0.34, 0.87, and 2.79 wt%, respectively.

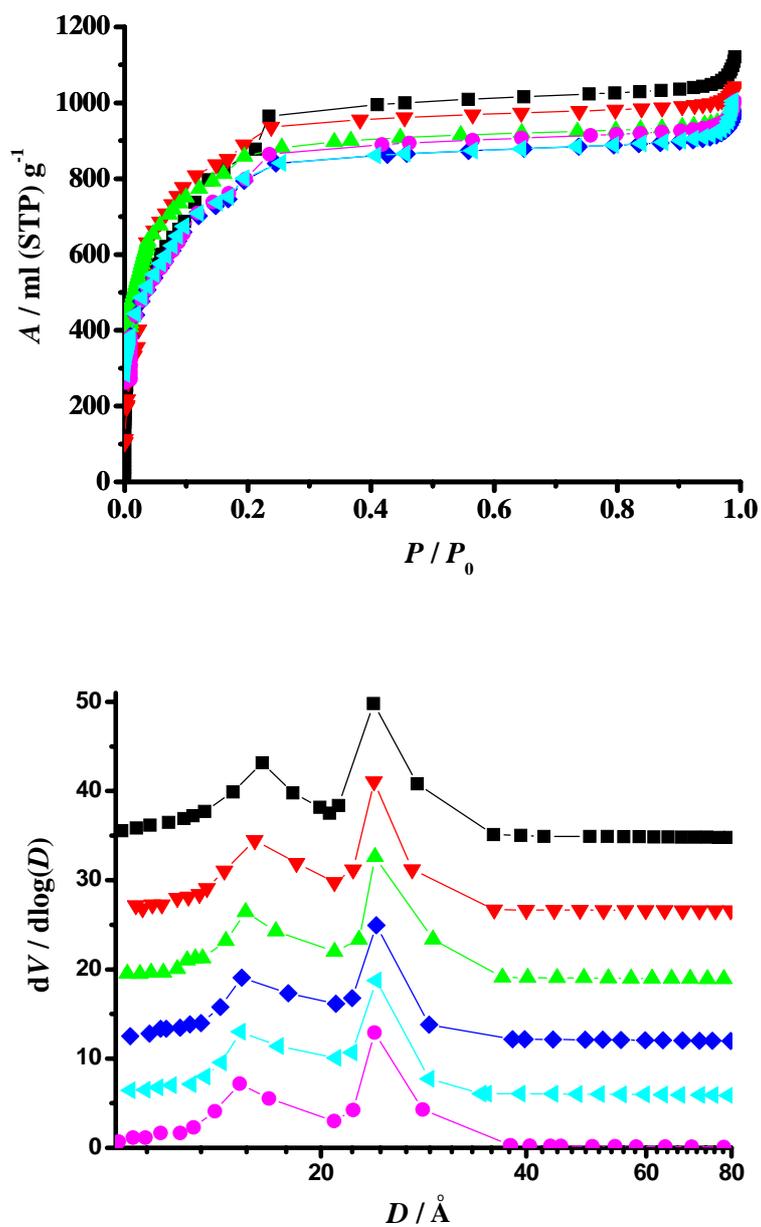
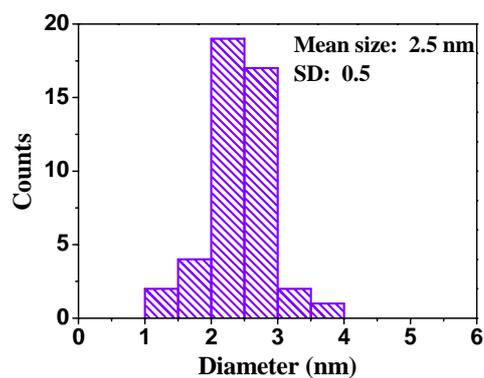
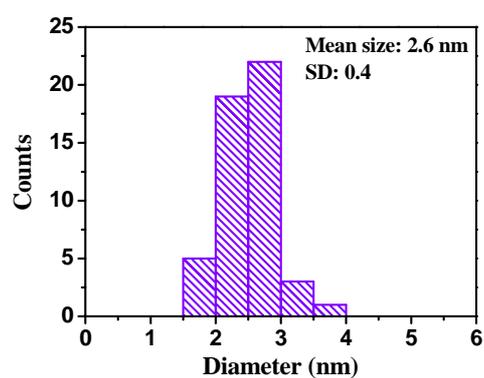


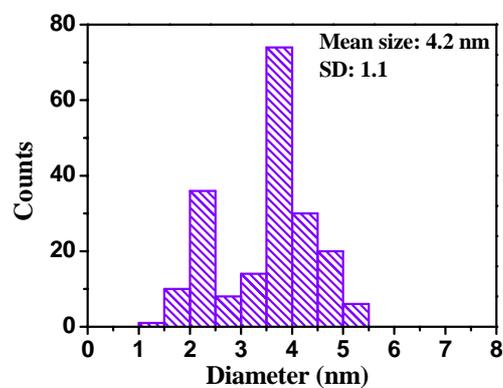
Fig. S2 Nitrogen adsorption isotherms at 77K (top) and pore-size distribution curves with adsorption volume V and pore diameter D (bottom) of the as-synthesized MIL-101 (■) and Pd@MIL-101 with Pd loading of 0.11 (▼), 0.22 (▲), 0.34 (◆), 0.87 (◄), and 2.79 wt% (●), respectively.



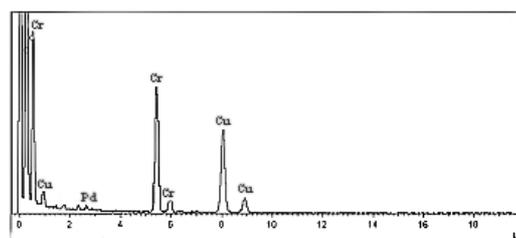
(a)



(b)



(c)



(d)

Figure S3. Size distributions of Pd NPs on the 0.11 wt% (a, b) and 0.87 wt% (c) Pd@MIL-101 before (a, c) and after (b) reaction. (d), EDX pattern of the 0.11 wt% sample before reaction.

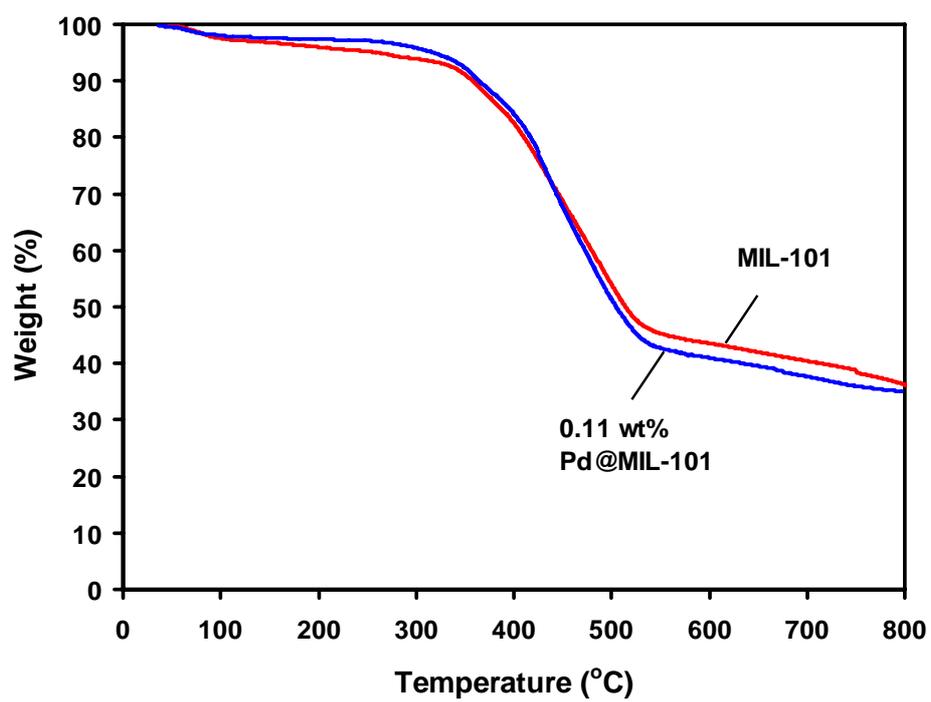


Fig. S4 TGA curves for MIL-101 and 0.11 wt% Pd@MIL-101.

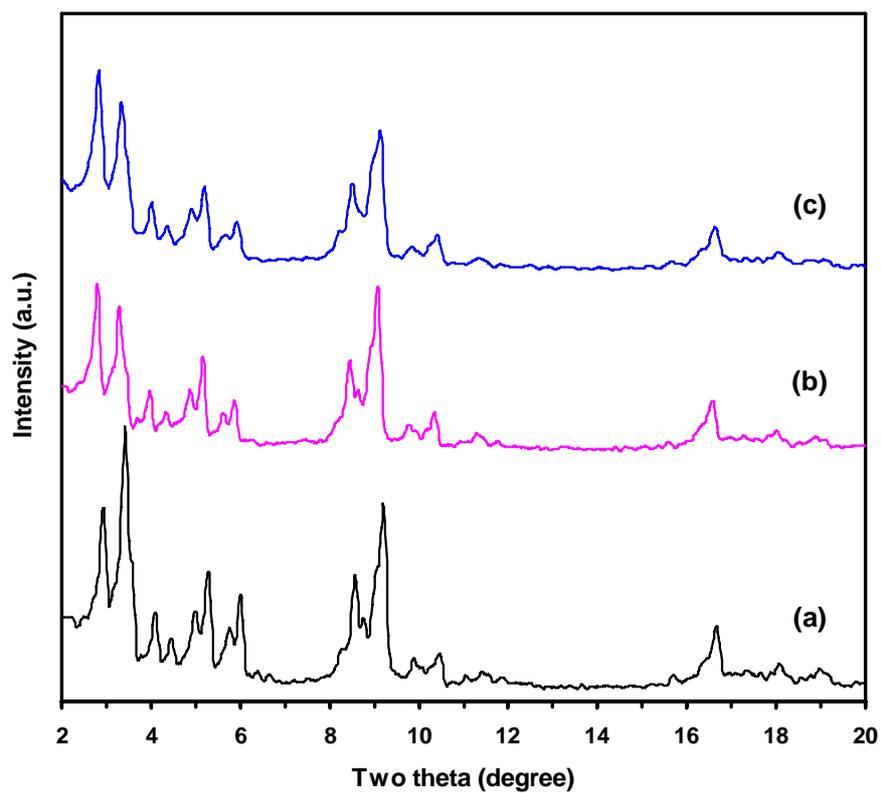


Fig. S5 XRD patterns of MIL-101 samples. (a) MIL-101, as-synthesized, (b) 0.11 wt% Pd@MIL-101, before reaction, (c) 0.11 wt% Pd@MIL-101, after 5 runs of catalysis.