

Chromium Based Metal-Organic Framework MIL-101 Decorated Palladium Nanoparticles for the Methanolysis of Ammonia-Borane

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(ELECTRONIC SUPPLEMENTARY INFORMATION)

Materials

Chromium(III) nitrate nonahydrate, terephthalic acid ($C_8H_6O_4$), methanol (CH_3OH), dimethylformamide (C_3H_7NO) ammonia-borane (NH_3BH_3), palladium(II) nitrate dihydrate ($Pd(NO_3)_2 \cdot 2H_2O$), *n*-hexane (C_6H_{14}) were purchased from Sigma-Aldrich[®]. Methanol was distilled over Mg and then, transferred into a nitrogen atmosphere dry-box before use ($O_2 < 5$ ppm, $H_2O < 1$ ppm). Deionized water was distilled by water purification system (Milli-Q Water Purification System). All glassware and Teflon coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with distilled water before drying in an oven at 323 K.

Characterization

Pd contents of the samples were determined by ICP-MS (Perkin Elmer DRC II model) after each sample was completely dissolved in a mixture of HNO_3/HCl ($v/v = 1/3$). XPS analysis was performed on a Physical Electronics 5800 spectrometer equipped with a hemispherical analyzer and using monochromatic Al $K\alpha$ radiation (1486.6 eV, the X-ray tube working at 15 kV, 350W and pass energy of 23.5 keV). The X-ray diffraction (XRD) pattern was recorded on a MAC Science MXP 3TZ diffractometer using Cu $K\alpha$ radiation (wavelength 1.5406\AA , 40 kV, 55 mA). Bright field transmission electron microscopy (BFTEM) was performed on a JEM-2010F microscope (JEOL) operating at 200 kV. A small amount of powder sample was placed on the copper TEM grid. Samples were examined at magnification between 100 and 400 K. Field emission scanning electron microscope (SEM) images were taken using a JEOL JSM- 5310LV at 15 kV and 33 Pa in a low-vacuum mode without metal coating on aluminum support. The nitrogen adsorption/desorption experiments were carried out at 77 K using a NOVA 3000 series (Quantachrome Instruments) instrument. The sample was outgassed under vacuum at 373 K for 3 h before the adsorption of nitrogen. FTIR spectra were taken from KBr pellet by using Nicolet Magna-IR 750 spectrometer using Omnic software ^{11}B NMR spectra were recorded on a Bruker Avance DPX 400 MHz spectrometer (128.2 MHz for ^{11}B) by using $BF_3(C_2H_5)_2O$ as external reference for ^{11}B NMR chemical shifts.

Catalysts Preparation

MIL-101 was synthesized according to literature report [1]. In the activation of MIL- 101, after the synthesis, MIL-101 solids were separated from water using a centrifuge (5000 rpm, 10

min) and washed with water, methanol and acetone. The final suspension in acetone was centrifuged and separated solid was placed in DMF (20.0 mL) and the suspension was sonicated for 10 min and kept at 343 K for 12 h. The resulting solid powder was separated by centrifugation repeatedly washed with methanol and acetone, activated by drying at 423 K for 12 h under vacuum (10^{-3} Torr). Then, 100 mg MIL-101 was suspended in 10 mL dry *n*-hexane as hydrophobic solvent and the mixture was sonicated for 15 min. Next, taken on magnetic stirrer and stirred at 700 rpm at room temperature. After stirring of 1 h, 1.0 mL aqueous $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (2.4 mg, 22.5 μmol Pd) was added dropwise over 10 min. with constant stirring for 2 hours. After centrifugation (6000 rpm, 10 min.), copious washing with water (3×10 mL), the isolated sample in powdered form was dried in a vacuum oven (10^{-1} Torr) at 343 K for 3 h. Next, the powder form of Pd(II)@MIL-101 was added into 15.0 mL OAm solution and heated to 383 K in 25 min. and kept at this temperature for 1 h under N_2 atmosphere. Next, this mixture was cooled to room temperature and Pd@MIL-101 was separated by centrifugation (10000 rpm for 10 min.) the isolated sample in powdered form was dried in a vacuum oven (10^{-1} Torr) at 343 K for 3 h. Pd@MIL-101 powders form were put into a quartz tube which was placed in furnace and connected to vacuum (10^{-4} Torr). Thus the sample was dehydrated with the following heating schedule, using a Protek series temperature controller: 0.5 h from 298 to 373 K, 1 h at 373 K, 2 h from 373 to 473 K and 2 h at 473 K. After thermal treatment the sample inside the quartz tube was cooled down to room temperature, sealed and transferred into the glove box ($\text{O}_2 < 5$ ppm, $\text{H}_2\text{O} < 1$ ppm). Pd/MIL-101 catalyst was obtained by the conventional impregnation and subsequent reduction steps. Typically, 5.0 mL aqueous $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (2.4 mg, 22.5 μmol Pd) solution and activated MIL powders (100 mg) is mixed for 3 h. Then, the fresh 1.0 mL aqueous solution of NaBH_4 (16 mg, 0.43 mmol) was added to this mixture and the resulting solution was stirred for half an hour under ambient conditions. After centrifugation (6000 rpm, 5 min), copious washing with water (3×20 mL), filtration, and drying in oven at 373 K, Pd/MIL-101 catalyst was obtained as a dark gray powder. The dehydration of Pd/MIL-101 was done by following the same procedure with that of Pd@MIL-101.

Catalytic Methanolysis of AB

The catalytic methanolysis of AB was surveyed by volumetric measurement of the rate of hydrogen evolution. The volume of released gas during the reaction was monitored using a gas

burette through water displacement. Beforehand starting, a jacketed one-necked Schlenk tube (20.0 mL), of which the temperature was adjusted by circulating water through the jacket from a constant temperature bath, containing a Teflon-coated stirring bar was placed on a magnetic stirrer. In a typical catalytic activity test, Pd@MIL-101 catalyst (0.56 μmol Pd) was weighed and transferred into the Schlenk, and then 8.0 mL dry methanol was added into this Schlenk followed by rigorous stirring for 15 min. to achieve a thermal equilibrium. Next, 2.0 mL of methanol solution of AB (150 mM in 10.0 mL CH_3OH) was added into the reaction flask via its septum using a 3.0 mL gastight syringe, and the catalytic reaction was started ($t = 0$ min) by stirring the mixture at 900 rpm.

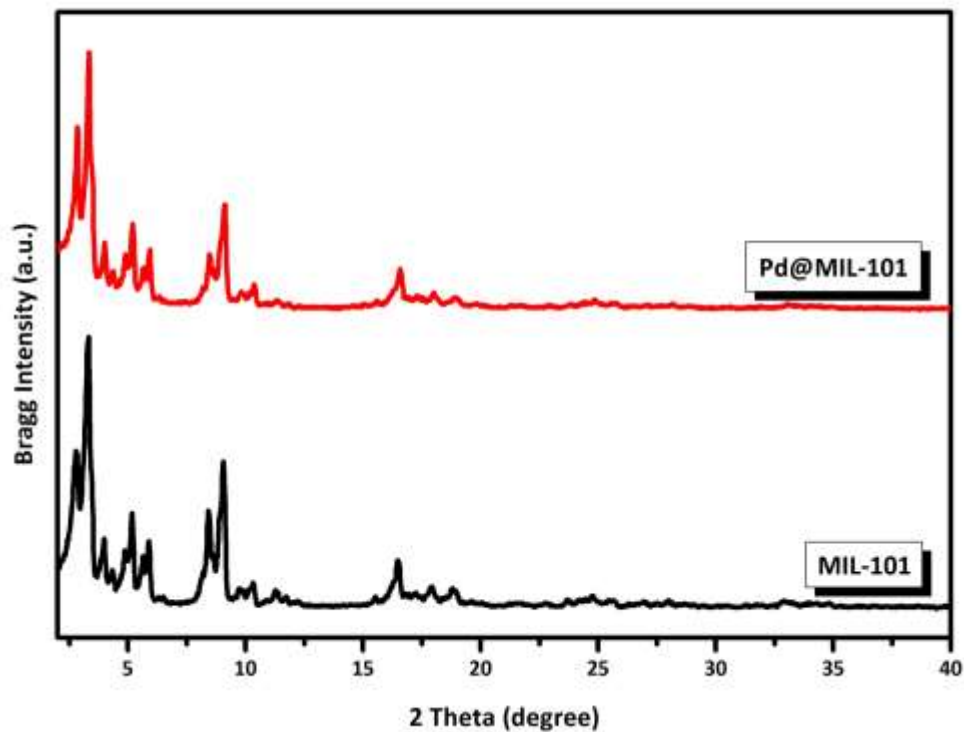


Fig. S1 P-XRD patterns of MIL-101 and Pd@MIL-101 in $2\theta = 3\text{-}40^\circ$.

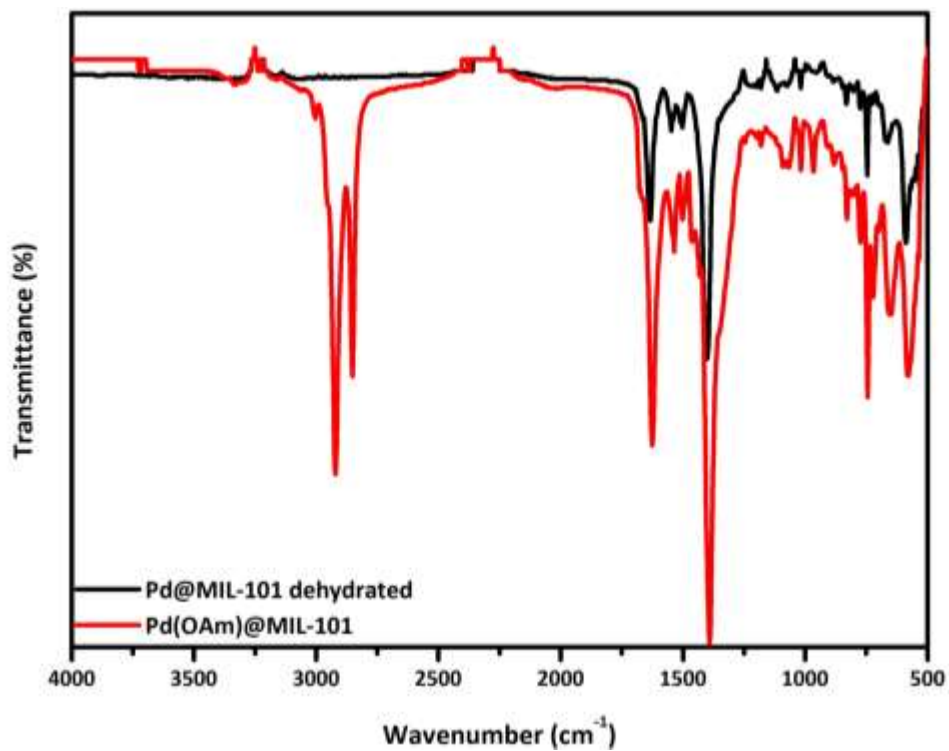


Fig. S2 FTIR spectra of Pd(OAm)@MIL-101 and Pd@MIL-101 after dehydration and ligand removal in 500-4000 cm^{-1} range.

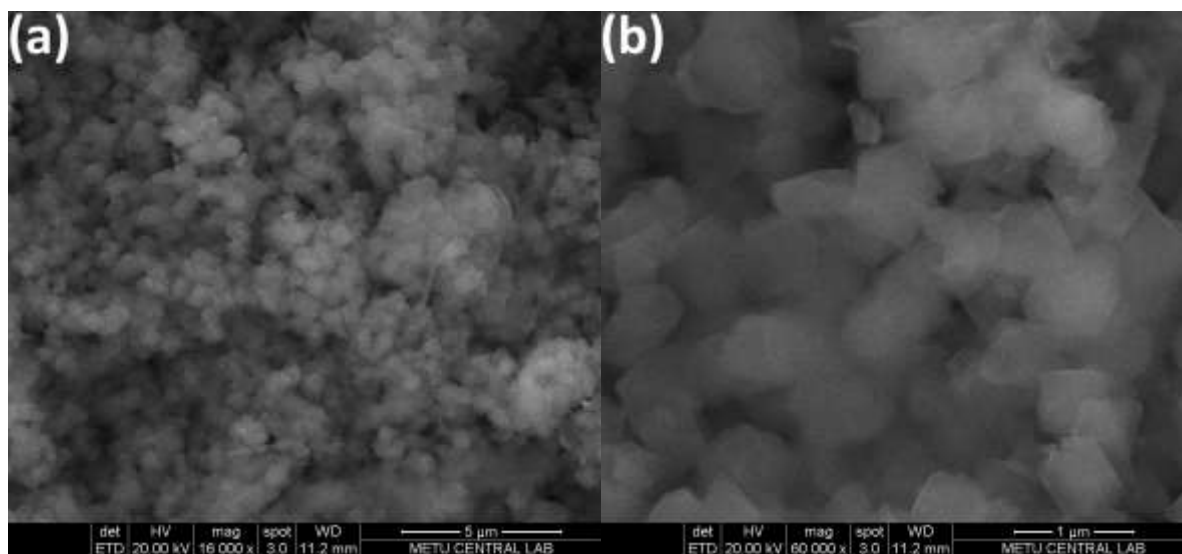


Fig. S3 FE-SEM images of Pd@MIL-101 catalyst in different magnifications.

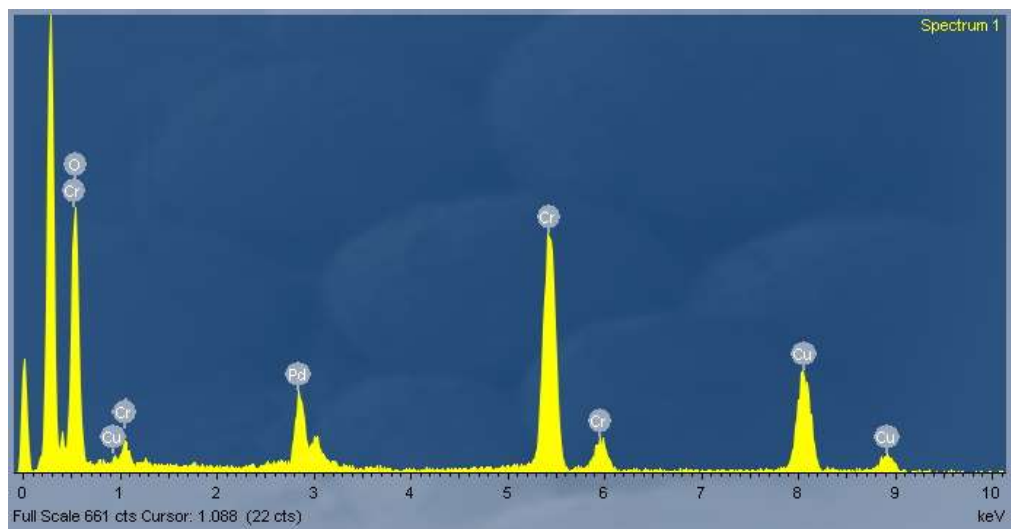


Fig. S4 STEM-EDX spectrum of Pd@MIL-101 catalyst.

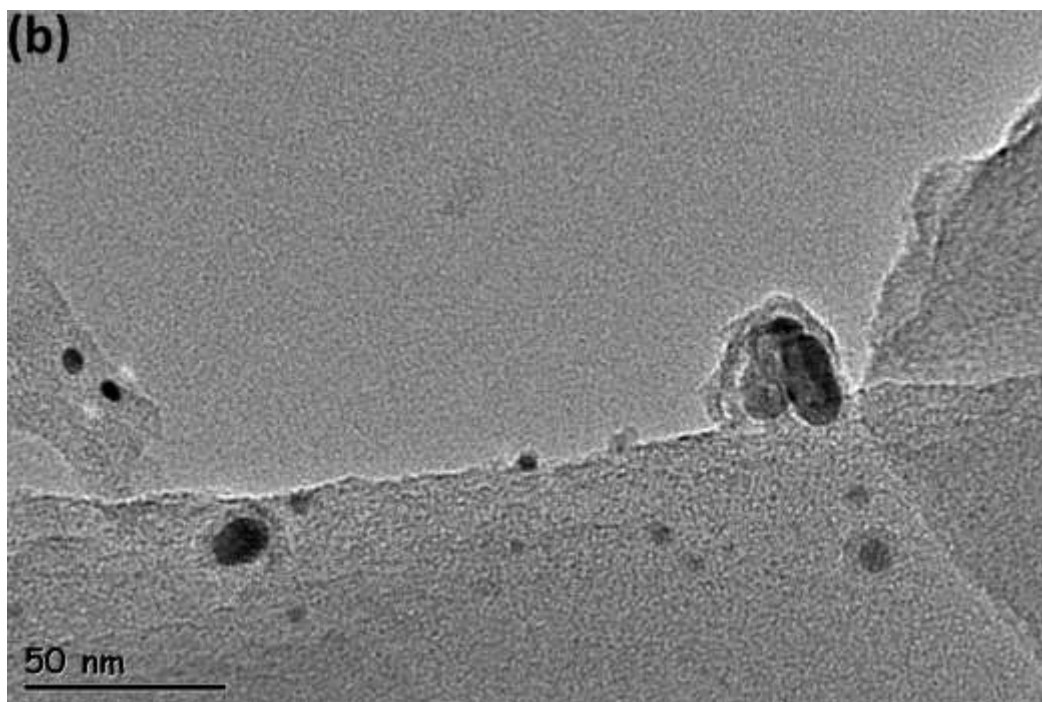
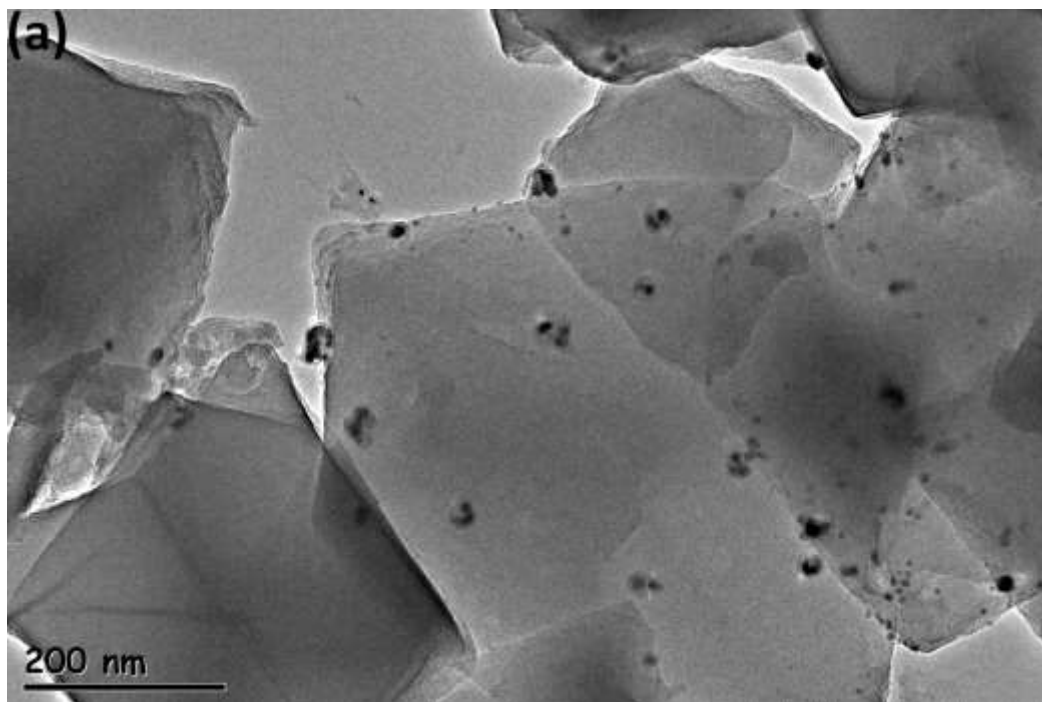


Fig. S5 BFTEM images of Pd/MIL-101 catalyst prepared by the conventional impregnation and borohydride reduction method.

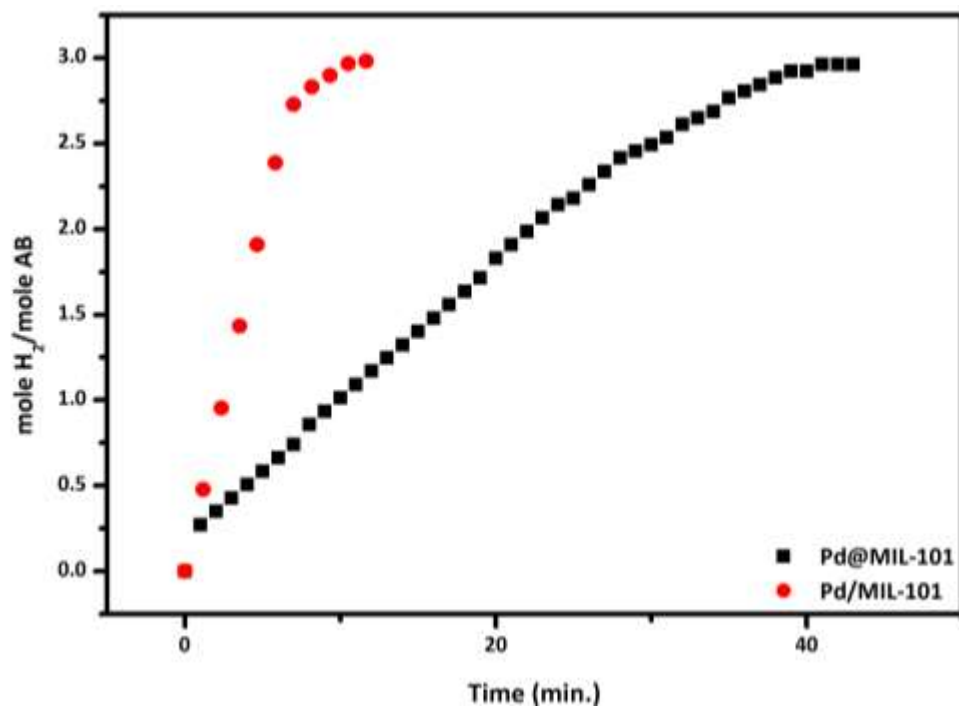


Fig. S6 Plot of the stoichiometric ratio of H₂ generated to AB versus time for Pd@MIL-101 and Pd/MIL-101 (in both 0.556 mol Pd) catalyzed methanolysis of AB (1.5 mmol) starting at 298 K.

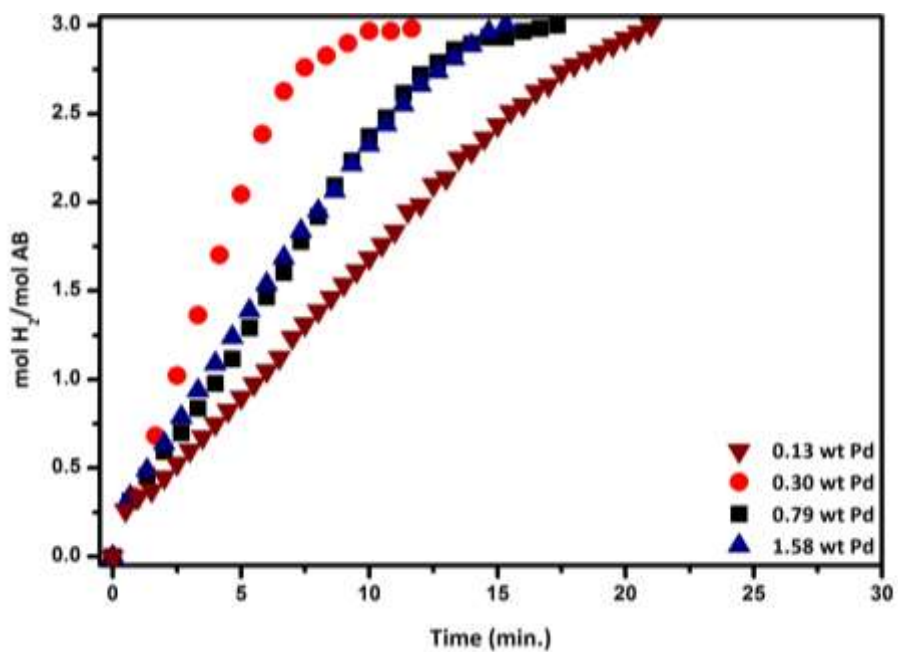


Fig. S7 Plot of the stoichiometric ratio of H₂ generated to AB versus time for Pd@MIL-101 catalyzed methanolysis of AB starting with various Pd loadings (wt % 0.13, 0.30, 0.79 and 1.58 in all n_{Pd} = 0.556 μmol) at 298 K.

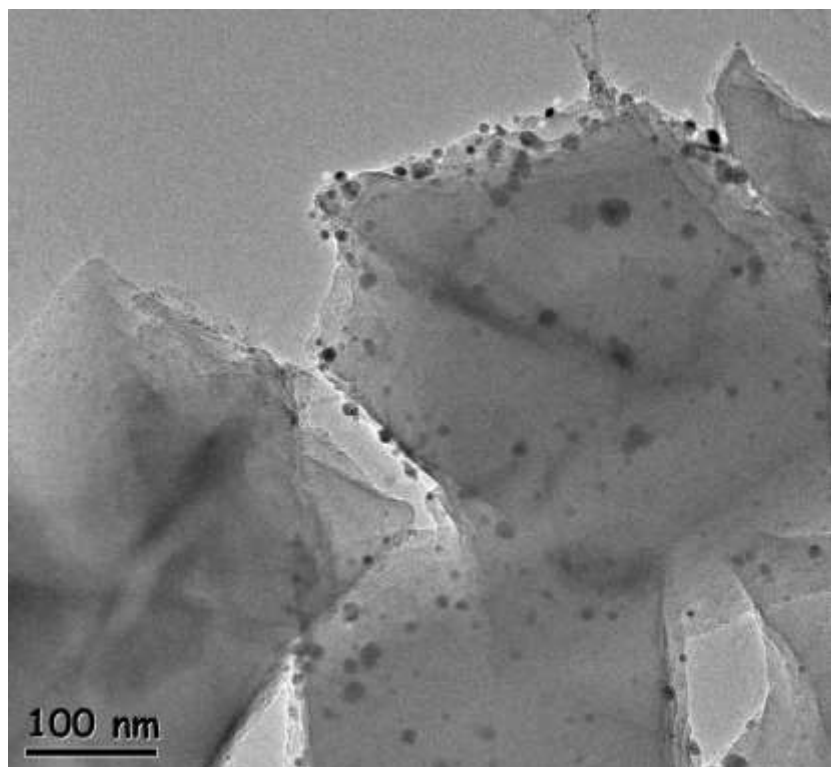


Fig. S8 BFTEM images of Pd@MIL-101 catalyst containing 1.58 wt % Pd.

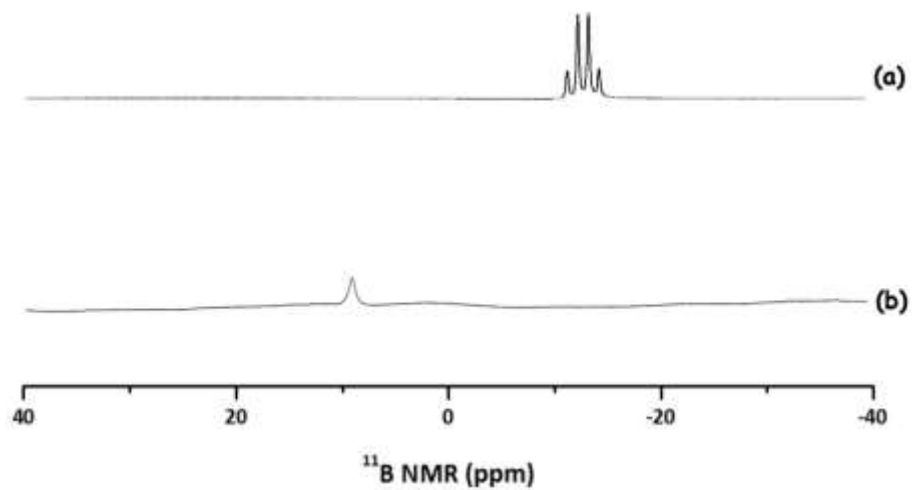


Fig. S9 ^{11}B NMR spectra of (a) fresh AB solution and (b) aliquot taken at the end of Pd@MIL-101 catalyzed methanolysis of AB.

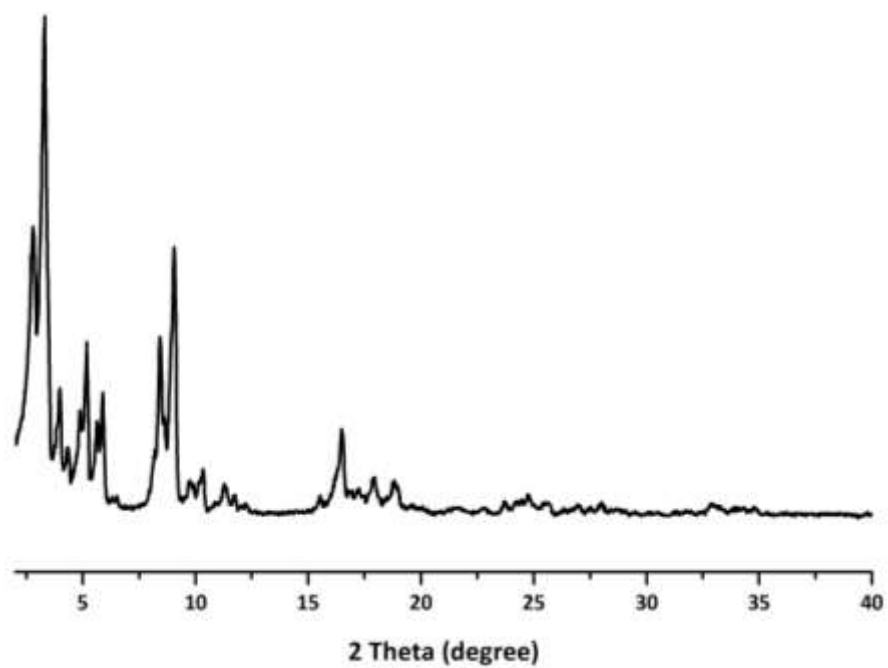


Fig. S10 P-XRD pattern of Pd@MIL-101 catalyst recovered from 5th catalytic recycle.

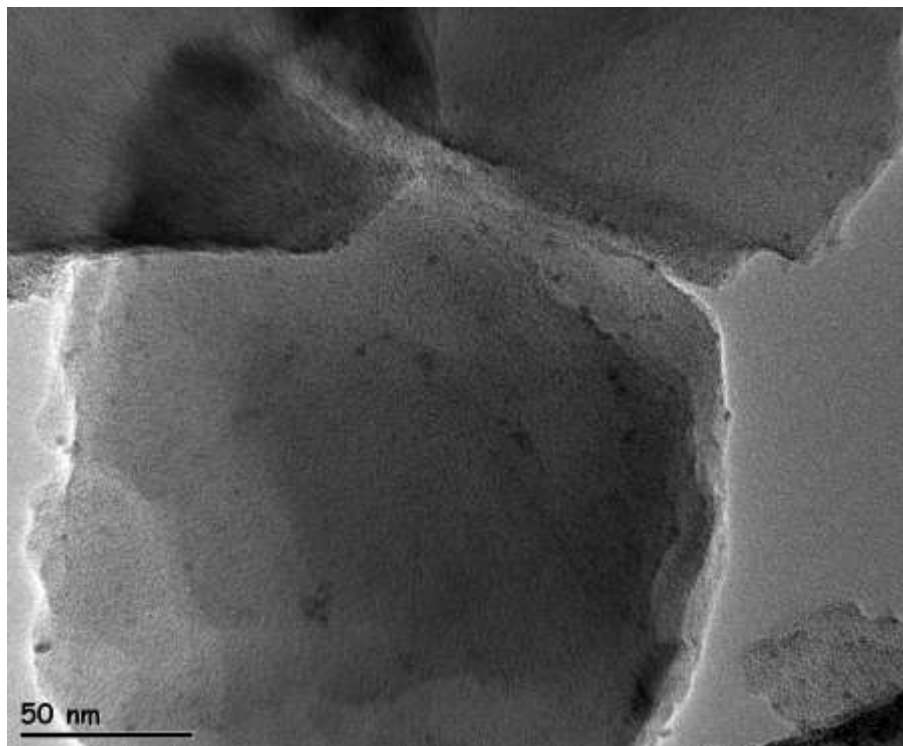


Fig. S11 BFTEM image of Pd@MIL-101 catalyst recovered from 5th catalytic cycle.

Calculation of Initial TOF Value

The *initial* TOF values were calculated by considering the region where 20 % conversion is achieved [2]. For example *initial* TOF value at room temperature was calculated as given below.

- 150 mM AB in 10.0 mL MeOH solution equals to 1.5 mmol AB and generated 4.5 mmol H₂ in the catalytic methanolysis reaction that corresponds to 100.8 mL H₂ and 20 % of its equals to 20.16 mL H₂,
- According to graph 0.6 mol H₂/mol AB (~ 20.16 mL H₂) generated at 1.5 min,
- Pd@MIL-101 contains 0.556 μmol Pd,
- Initial TOF = $(20.16/22400)\text{mol} / (0.556 \times 10^{-6} \text{mol})(1.5 \text{ min}) = 1080 \text{ min}^{-1}$

Table S1. Comparison of the catalytic performance data in terms of activity for Pd@MIL-101 nanocatalyst with the prior best heterogeneous catalyst systems (TOF > 100 min⁻¹) reported for the room temperature methanolysis of AB.

Entry	Catalyst	Activity (TOF)	Reference
1	RuCl ₃	150	10
2	RhCl ₃	100	10
3	Rh/HAp	147	22
4	AgPd alloy	366.4	14
5	Rh/PC-COF	505	17
6	Rh-PRO/C	1035	18
7	Rh/CeO ₂	144	19
8	Pd/GNS	102	20
9	Rh/Al ₂ O ₃	218	21
10	Pd@MIL-101	1080	this study

References

- [1] L. Bromberg, Y. Diao, H. Wu, S.A. Speakman, T.A. Hatton, Chem. Mater 24 (2012) 1664.
- [2] Z. L. Wang, J. M. Yang, Y. Ping, W. T. Zheng, Q. Jiang, Angew. Chem. Int. Ed. 52 (2013) 4406.