Electronic Supplementary Information

One-Pot Tandem Catalysis over Pd@MIL-101: Boosting Efficiency of Nitro Compound Hydrogenation by Coupling with Ammonia Borane Dehydrogenation

Qihao Yang,[a,‡] Yu-Zhen Chen,[a,‡] Zhiyong U. Wang,[b] Qiang Xu,[c] and Hai-Long Jiang*,[a]

[a]*Hefei National Laboratory for Physical Sciences at the Microscale, CAS Key Laboratory of Soft Matter Chemistry, Collaborative Innovation Center of Suzhou Nano Science and Technology, Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P.R. China*

[b] *Department of Chemistry and Physics, Troy University, Troy, AL 36082, USA.*

[c]*National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka 563-8577, Japan*

‡*These authors contributed equally to this work.*

* *To whom correspondence should be addressed.*

E-mail: jianglab@ustc.edu.cn

1. Materials and Instrumentation.

All chemicals were purchased from commercial sources and used without further treatment: chromium(III) nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$, Sigma-Aldrich, 99%), 1,4-benzene dicarboxylic acid (TCI, >99.0%), aqueous HF (Aladdin Industrial Inc., 40%)，palladium(II) nitrate solution ($Pd(NO_3)_2$, ~5wt.% Pd basis, Shaanxi Kaida Chemical Engineering Co., Ltd), ammonia borane (NH_3BH_3, Sigma-Aldrich, 90%), anhydrous *n*-hexane (Sinopharm Chemical Reagent Co., Ltd., ⩾97%), methanol (CH_3OH, Sinopharm Chemical Reagent Co., Ltd., >99%), nitrobenzene (Sinopharm Chemical Reagent Co., Ltd., CP), nitromethane (Aladdin Industrial Inc., AR), nitroethane (Aladdin Industrial Inc., 99%), 2-nitrotoluene (Aladdin Industrial Inc., 99%), 3-nitrotoluene (Aladdin Industrial Inc., 98%), 4-nitrotoluene (Aladdin Industrial Inc., 99%), 4-nitrobenzyl alcohol (Energy Chemical, 98%), 4-nitrophenol (Aladdin Industrial Inc., AR), 2-nitroaniline (Aladdin Industrial Inc., 99%), 3-nitroaniline (Aladdin Industrial Inc., 98%), 4-nitroaniline (Aladdin Industrial Inc., AR), 1,3-dinitrobenzene (Aladdin Industrial Inc., CP) and 4-fluoronitrobenzene (Aladdin Industrial Inc., 98%). De-ionized water with the specific resistance of 18.25 MΩ·cm was obtained by reversed osmosis followed by ion-exchange and filtration (Cleaned Water Treatment Co., Ltd., Hefei). The transmission electron microscopy (TEM) was acquired on JEOL-2010 with an electron acceleration energy of 200 kV. Powder X-ray diffraction patterns (PXRD) were carried out on a Japan Rigaku SmartLab^{TM} rotation anode X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.54 Å). The nitrogen sorption isotherms were measured by using an automatic volumetric adsorption equipment (Micrometritics ASAP 2020). Prior to nitrogen adsorption/desorption measurement, the samples were dried for 12 h at 433 K under vacuum. The content of Pd in Pd@MIL-101 was quantified by an Optima 7300 DV inductively coupled plasma atomic emission spectrometer (ICP-AES). The catalytic reaction products were analyzed and identified by gas chromatography (GC, Shimadzu 2010 Plus with a 0.25 mm × 30 m Rtx-5 capillary column).

2. Catalyst Preparation.

Preparation of MIL-101: MIL-101 were synthesized and purified according to the reported procedures.[1] A typical synthesis involves a solution containing $Cr(NO_3)_3 \cdot 9H_2O$ (4.33 g, 10.8 mmol), 1,4-benzene dicarboxylic acid (1.8 g, 10.8 mmol), de-ionized water (52 mL), aqueous HF (0.3 mL, 1.5 mmol). The mixture was introduced into a Teflon-lined autoclave and heated for 8 h at 473 K in an oven under static condition. To remove organic species trapped within the pores, MIL-101 was activated in boiling water overnight following purified twice by in ethanol at reflux temperature for 24 h and washed with hot ethanol, and was further purified by NH_4F solution. The sample was dried at 433 K for 12 h under dynamic vacuum prior to the further use.

Preparation of Pd^{2+}@MIL-101: A typical preparation procedure is described as follows: 200 mg of activated MIL-101 was suspended in hydrophobic solvent of dry *n*-hexane (40 mL). The mixture was sonicated for 30 min to make sample evenly dispersed in the hexane. To which 0.30 mL of hydrophilic aqueous $Pd(NO_3)_2 \cdot 2H_2O$ (with Pd^{2+} amount of 0.019 mmol) was pumped dropwise into the flask under continuous vigorous stirring and the mixture were stirred for another 3 h. After stirring, the green powder settled down to the bottom of the flask samples, which can be separated through the dumping of supernatant fluid and was simply dried in air at room temperature. The synthesized sample was further dried overnight at 433 K under dynamic vacuum.

Preparation of Pd@MIL-101: A certain amount of Pd^{2+}@MIL-101 was stirred in 20 mL mixture solution of methanol and water (v:v = 2:3) with 30 mg ammonia borane and 0.4 mmol nitro compounds. The Pd^{2+} was rapidly reduced in situ during the hydrolytic/methanolytic dehydrogeneration of ammonia borane to give Pd@MIL-101.

3. Catalytic Activity Characterization.

Assessment of the catalytic performance of Pd@MIL-101 for ammonia borane dehydrogenation reaction only: In general, a mixture of 34 mg Pd^{2+}@MIL-101, 0.4 mmol nitro compound, 8 mL methanol and 12 mL de-ionized water was placed in a two-necked round-bottomed flask (50 mL) under magnetic stirring. A gas burette filled with water was connected to the reaction flask to measure the volume of hydrogen evolved. The reaction started when 30 mg NH_3BH_3 was added into the flask. The volume of the evolved hydrogen gas was monitored by recording the displacement of water in the gas burette. The reaction was completed when there was no more gas generated. For the catalytic recycling/durability experiments, the same amount of NH_3BH_3 (30 mg) and nitro compounds were added into the flask to initiate the reaction.

Assessment of the catalytic performance of Pd@MIL-101 for the tandem reaction: Typically, a mixture of 34 mg Pd^{2+}@MIL-101, 30 mg NH_3BH_3 was placed in a two-necked round-bottomed flask (50 mL). The reaction started when the solution contained 8 mL methanol, 12 mL de-ionized water and 0.4 mmol nitro compound was added into the flask under magnetic stirring. For the catalytic recycling/durability experiments, the same amount of NH_3BH_3 (30 mg) and nitro compounds (0.4 mmol) were added into the flask to initiate the reaction. After the completion of the reaction with different time, 30 μL of the resultant mixture was taken to a mixed solvent with 1 mL H_2O and 1 mL ethyl acetate. Upon the adequate shaking, the above mixture was allowed to be centrifuged and the reaction product was extracted to the upper layer of ethyl acetate. Then, 600 μL of sample in the upper solution was detected by GC.

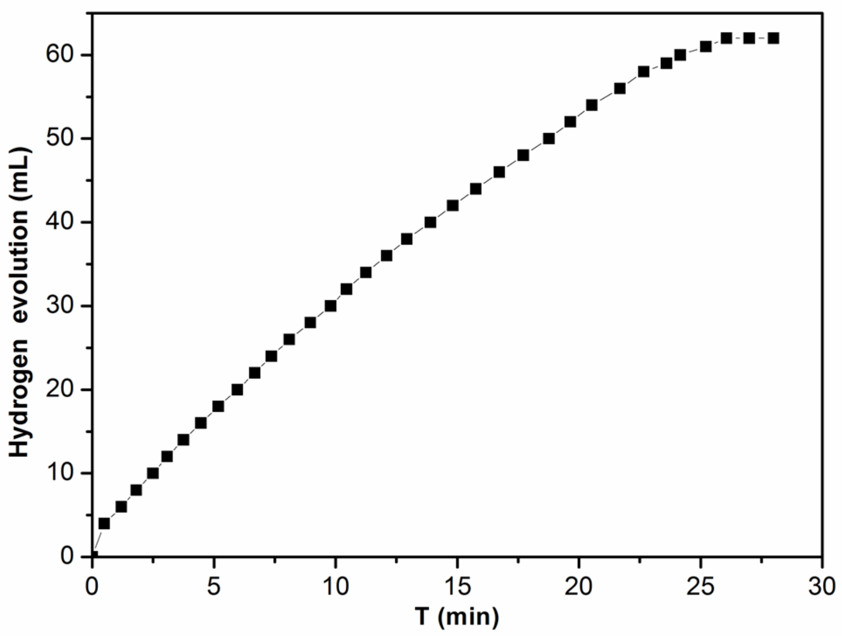

Fig. S1 Plot of time *versus* the volume of hydrogen generated from the hydrolysis of ammonia borane over Pd@MIL-101 in the mixed solvent of methanol/water (NH_3BH_3 = 0.875 mmol, Pd/NH_3BH_3 = 0.003 in molar ratio, MeOH = 8 mL, H_2O = 12 mL, T = 25 ^{o}C)

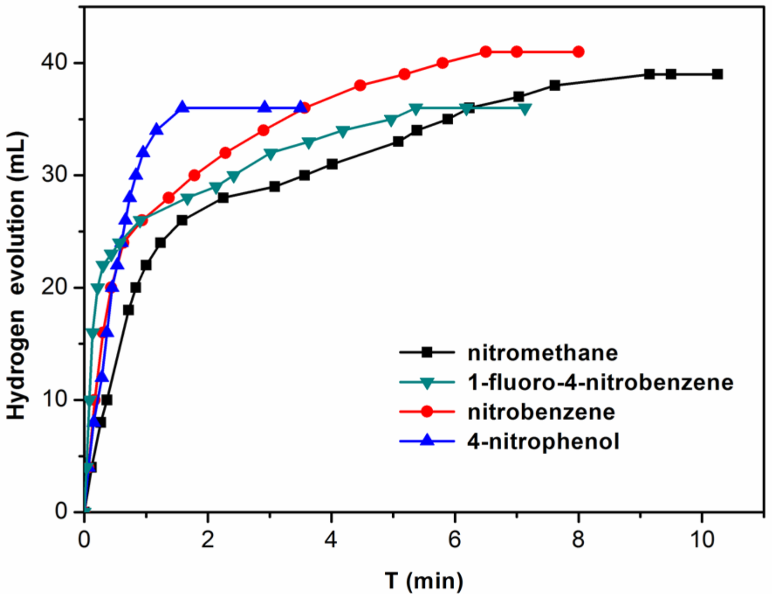

Fig. S2 Plots of time versus the volume of hydrogen generated from the hydrolysis of ammonia borane over Pd@MIL-101 in the mixed solvent of methanol/water (v/v = 2/3) containing different nitro compounds. (NH_3BH_3 = 0.875 mmol, Pd/NH_3BH_3 = 0.003 in molar ratio, Pd/nitro compound = 0.007 in molar ratio, R-NO_2 = 0.4 mmol, MeOH = 8 mL, H_2O = 12 mL, T = 25 ^{o}C).

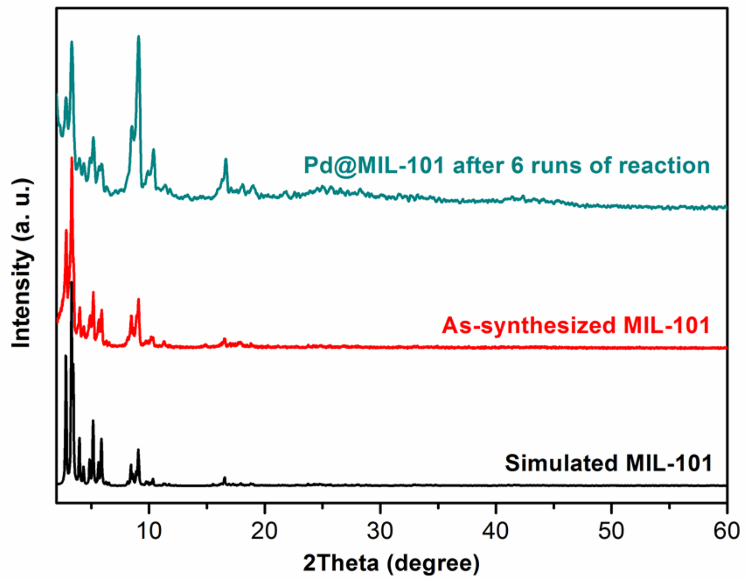

Fig. S3 Powder XRD patterns of simulated MIL-101, as-synthesized MIL-101 and Pd@MIL-101 after 6 cycles of tandem dehydrogenation of ammonia borane and hydrogenation of nitro compounds.

Table S1 Catalytic performance comparison between Pd@MIL-101 and previously reported Pd-based catalysts toward the nitrobenzene hydrogenation.

Catalyst	Temperature (^{o}C)	TOF ($mol_{Nitrobenzene} \cdot mol_{Pd}^{-1} \cdot min^{-1}$)	Ref.
Pd@MIL-101	25	97	This work
Fe_3O_4-NH_2-Pd	25	1.39	2
Pd-PEG	25	2.1	3
Pd/C	25	6.6	4
Pd-pol	25	1.9	5
Pd^0-in-UiO-67	25	0.56	6
$NiFe_2O_4$-DA-Pd	25	6.6	7
Pd-2-GNC	25	1.57	8
pPd Ns	25	32.51	9
$[ZnL_{0.42}L'_{0.58}Cl_2Pd_{0.58}(H_2O)_{1.16}]\cdot 9H_2O$	25	3.33	10
$Pd/Fe(OH)_x$	30	2.36	11
Pd/Al_2O_3	40	7.92	12
Pd/SiO_2	40	1.68	12
Pd/MgO	40	0.42	12
Pd/MWCNT-SA-3.6	40	32.03	12
$Pd@SiO_2$	45	31.17	13
SS-Pd	50	0.82	14
Pd/ZnO	90	69.91	15

References

1. G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040.

2. F. Zhang, J. Jin, X. Zhong, S. Li, J. Niu, R. Li and J. Ma, *Green Chem.*, 2011, **13**, 1238.

3. F. A. Harraz, S. El-Hout, H. M. Killa and I. A. Ibrahim, *J. Catal.*, 2012, **286**, 184.

4. K. Möbus, E. Grünewald, S. D. Wieland, S. F. Parker and P. W. Albers, *J. Catal.*, 2014, **311**, 153.

5. M. M. Dell'Anna, S. Intini, G. Romanazzi, A. Rizzuti, C. Leonelli, F. Piccinni and P. Mastrorilli, *J. Mol. Catal. A: Chem.*, 2014, **395**, 307.

6. L. Chen, H. Chen, R. Luque and Y. Li, *Chem. Sci.*, 2014, **5**, 3708.

7. D. Guin, B. Baruwati and S. V. Manorama, *Org. Lett.*, 2007, **9**, 1419.

8. S. Samanta and A. K. Nandi, *J. Phys. Chem. C.*, 2009, **113**, 4721.

9. X. Huang, Y. Li, Y. Chen, E. Zhou, Y. Xu, H. Zhou, X. Duan and Y. Huang, *Angew. Chem. Int. Ed.*, 2013, **52**, 2520.

10. G.-Q. Kong, S. Ou, C. Zou and C.-D. Wu, *J. Am. Chem. Soc.*, 2012, **134**, 19851.

11. C. Zhang, X. Cui, Y. Deng and F. Shi, *Tetrahedron*, 2014, **70**, 6050.

12. Z. Wang, H. Liu, L. Chen, L. Chou and X. Wang, *J. Mater. Res.*, 2013, **28**, 1326.

13. Y. Hu, K. Tao, C. Wu, C. Zhou, H. Yin and S. Zhou, *J. Phys. Chem. C.*, 2013, **117**, 8974.

14. A. K. Shil, D. Sharma, N. R. Guha and P. Das, *Tetrahedron Lett.*, 2012, **53**, 4858.

15. M. Hosseini-Sarvari and Z. Razmi, *Appl. Surf. Sci.*, 2015, **324**, 265.