Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Accelerated catalytic activity of Pd NPs supported on Amine-Rich Silica Hollow Nanospheres for Quinoline Hydrogenation

*Miao Guo, Can Li * and Qihua Yang**

General information

Synthesis of SiO_2 hollow nanospheres (HS). The SiO_2 HS was prepared with a modified mothod according our previous report.[1] Typically, 0.16 g of CTAB and 0.5 mL of $NH_3 \cdot H_2O$ (25-28%) was dissolved in 50 mL H_2O and 10 mL EtOH solution at 50 ^oC, then 0.16 ml TEOS (in 1 mL EtOH) was added to the transparent solution and the mixture was stirred for another 30 min. After that 0.24 mL of TEOS were added and stirred for 3 min. Then, 0.16 ml of BTME (Bis(trimethoxysilyl)ethane) (in 1ml EtOH) was added and the temperature was raised to 80 ^oC. The mixture was stirred at this temperature for 2h. After cooling down to the room temperature, the white solid were filtrated and calcinated to remove the CATB and organic moieties in air at 500 ^oC.

The calculation by Gaussian software. The structure of quinoline and 1, 2, 3, 4-tetraquinoline are optimized at the M06-2X level of density functional theory using the def2-SVP basis set on all atoms (C, H, O, N), incorporating solvation effects via the SMD continuum solvation model. NBO analyses are done with NBO version 3.1 implemented in Gaussian 09.

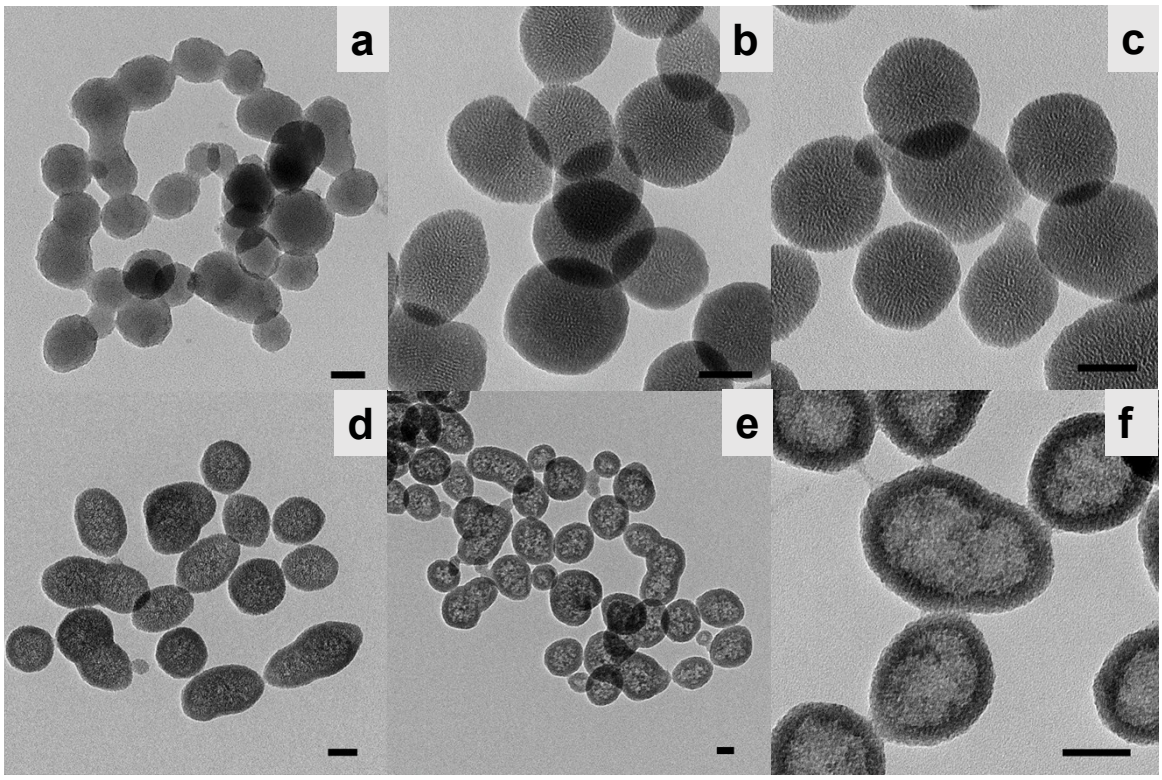

Figure S1. TEM images of (a) after adding TEOS for 2 min; (b) 50 ^{o}C, after adding APTES for 120 min; (c-f) 80 ^{o}C, for 5, 15, 30, 120 min, respectively (scale bar: 50 nm).

In the first stage, porous silica nanospheres with particle size of about 80 nm were formed. After the addition of APTES, the particle size of silica NPs increases to 110 nm. After the hydrothermal treatment at 80 ^{o}C, the nanospheres transform into hollow nanospheres.

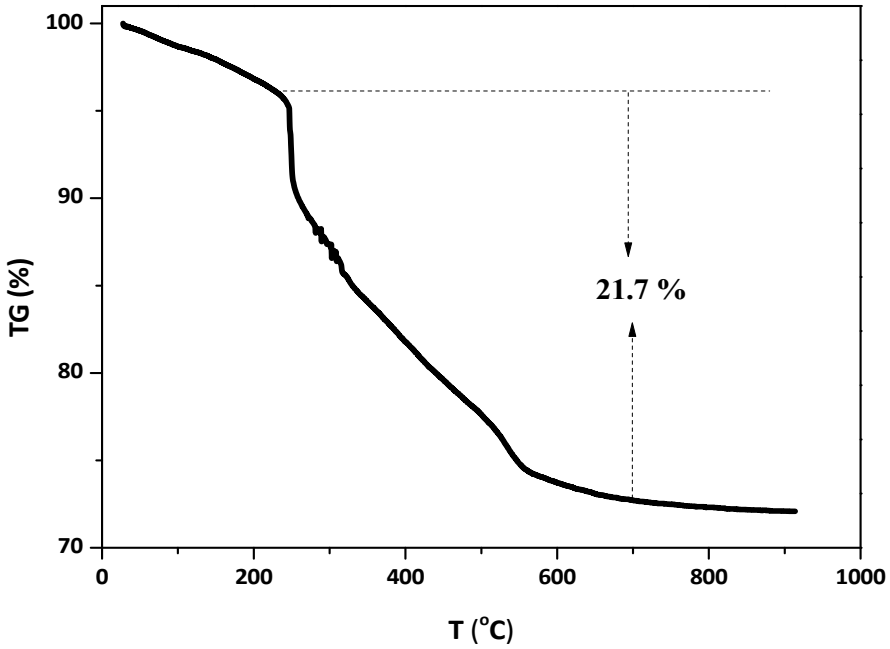

Figure S2. TG analysis of HS-NH_2.

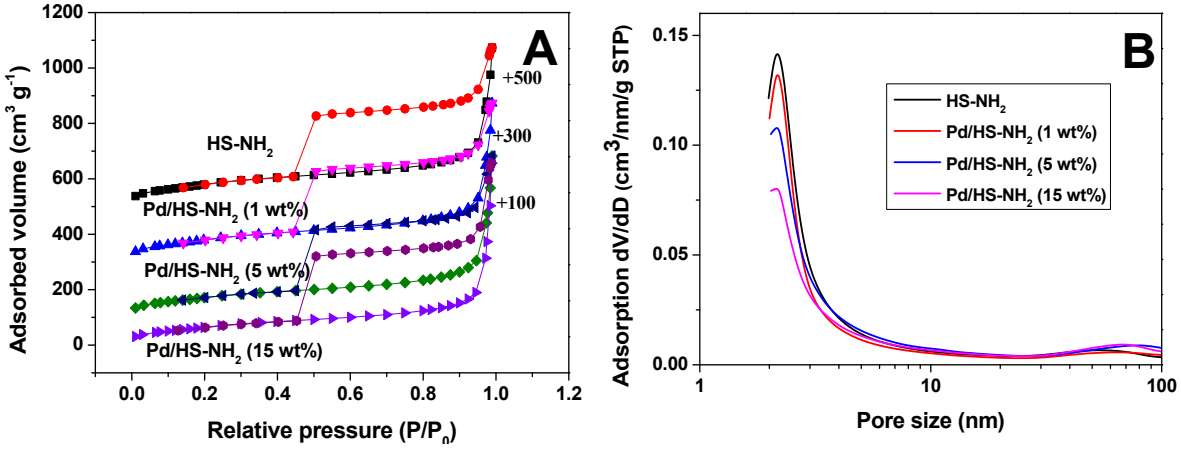

Figure S3. N_2 adsorption-desorption isotherm of HS-NH_2, Pd/HS-NH_2 (1 wt%), Pd/HS-NH_2 (5 %) and Pd/HS-NH_2 (15 wt%) (A) and corresponding pore size distribution (B).

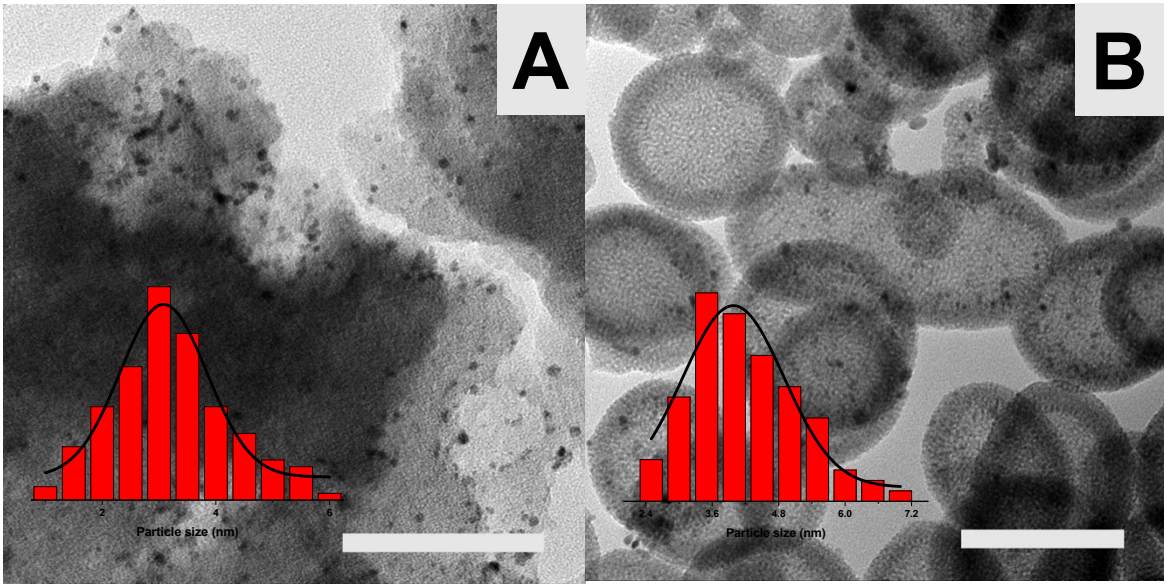

Figure S4. TEM images and particle size distribution of commercial Pd/C (5 wt%) (A) and Pd/HS (B) (scale bar: 100 nm).

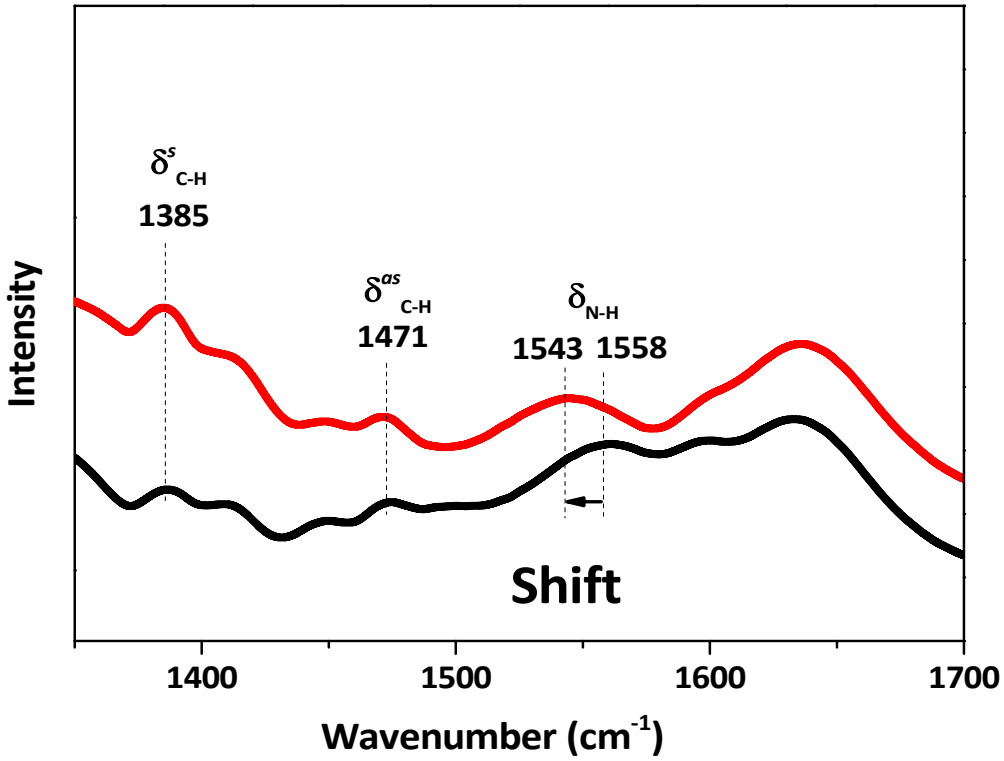

Figure S5. FT-IR spectra of (a) HS-NH_2 and (b) Pd/HS-NH_2 (5 wt%) in the range of 1300-1700 cm^{-1}.

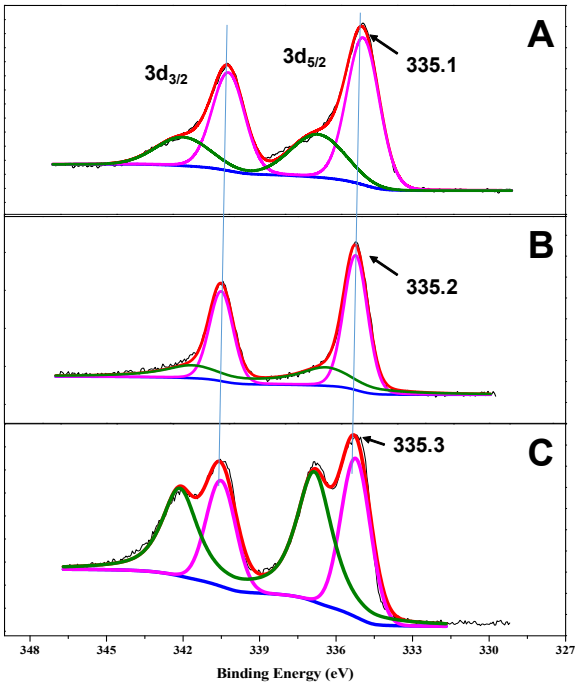

Figure S6. XPS spectra of Pd $3d_{3/2}$ and $3d_{5/2}$ core level for (A) Pd/HS-NH_2 (5 wt%), (B) Pd/HS (5 wt%) and (C) Pd/C (5 wt%).

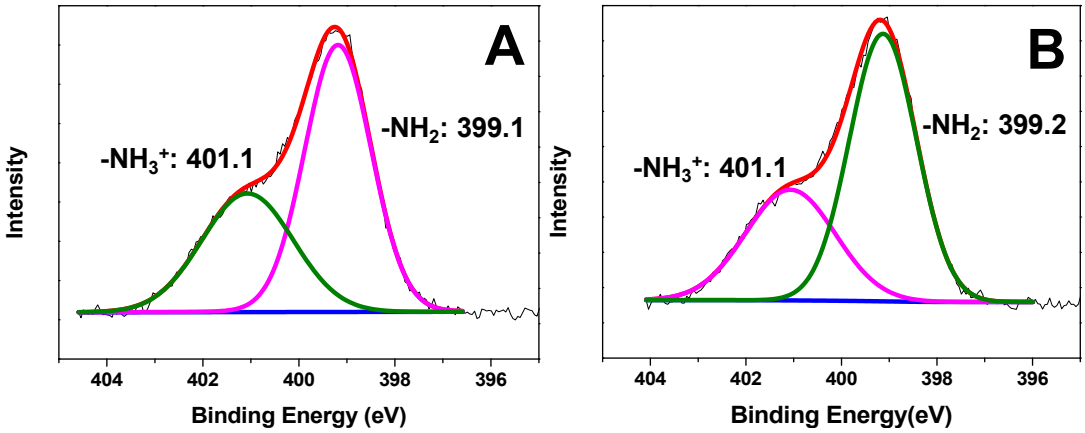

Figure S7. XPS spectra of N 1s core level for (A) Pd/HS-NH_2 (5 wt%) and (B) HS-NH_2.

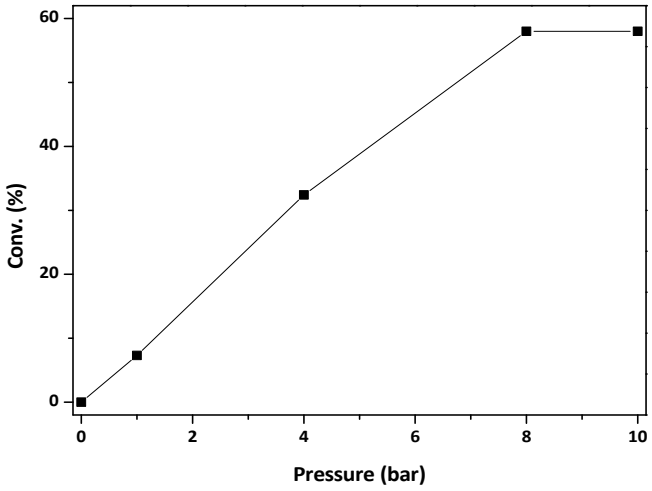

Figure S8. H_2 pressure effect of Pd/HS-NH_2 (5 wt%) on quinoline hydrogenation. Reaction conditions: quinoline 1 mmol, S/C=200, solvent 2mL cyclohexane, reaction time (1 h), reaction temperature (50 °C).

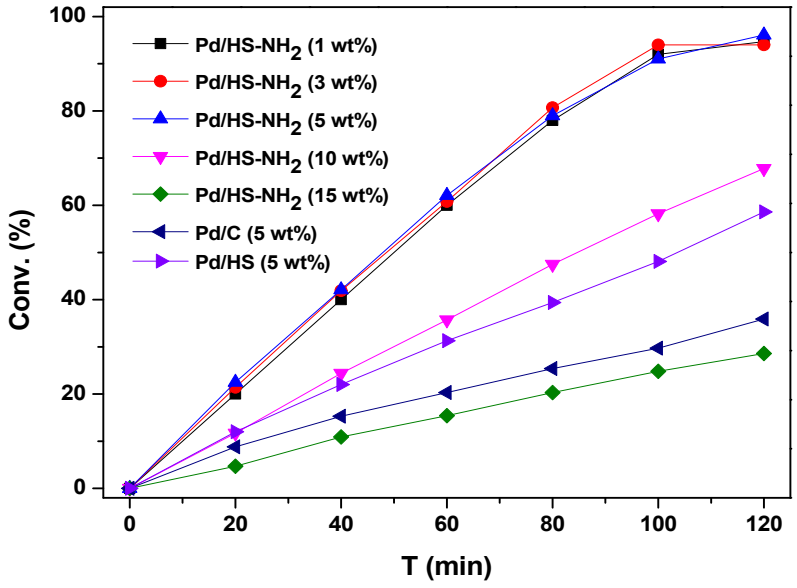

Figure S9. Kinetic curves of Pd/HS-NH_2 with different metal loading, Pd/C (5 wt%) and Pd/HS (5 wt%).

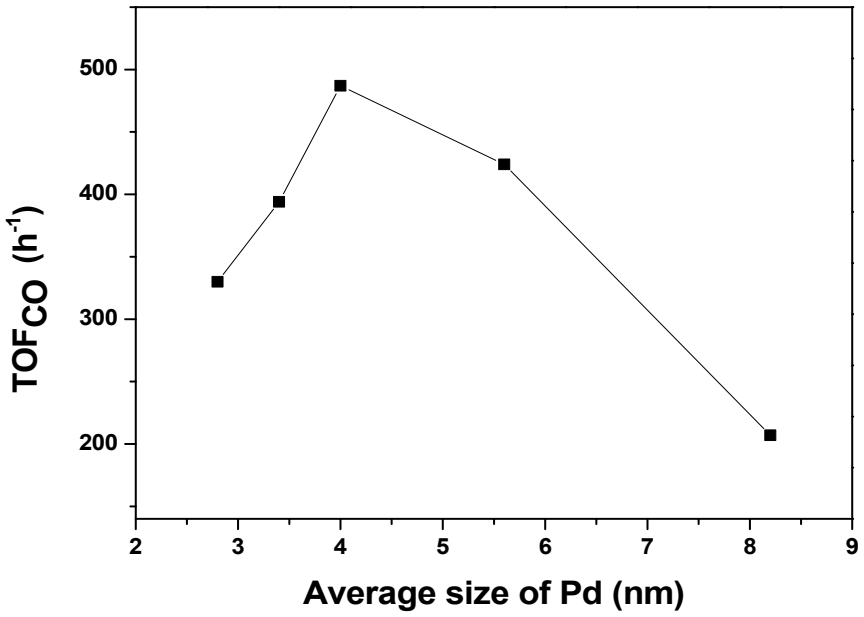

Figure S10. Plot of TOF_{CO} *vs* average size of Pd NPs.

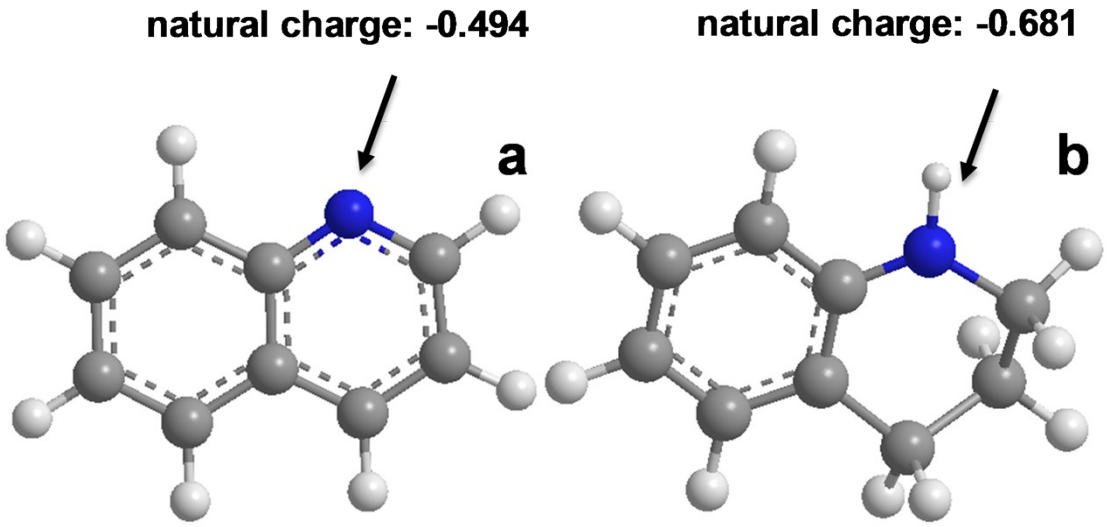

Figure S11. Quantum chemical calculations are carried out using Gaussian 09 program suite.[2]

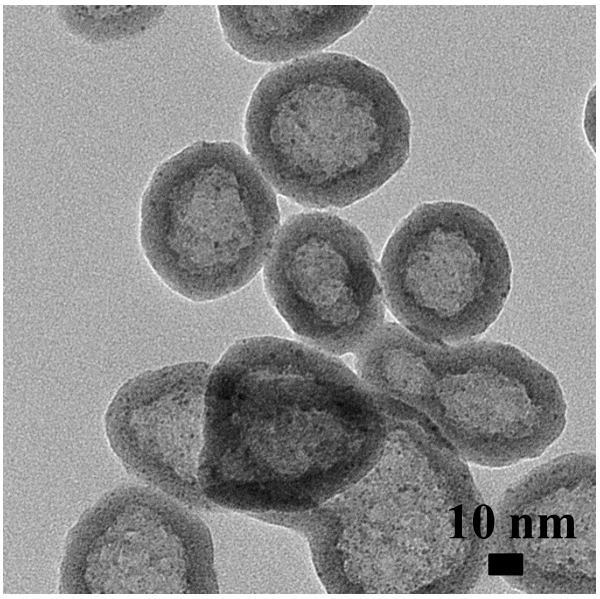

Figure S12. TEM image of Pd/HS-NH_2 (5 wt%) after 6th cycle.

Table S1. Physical parameters and element analysis of supports.

Support	BET/m^2 g^{-1}	Vt/cm^3 g^{-1}	Pore size/nm	C (%)	H (%)	N (%) (mmol g^{-1})
HS-NH_2	301	0.54	2.2	11.30	2.32	5.18 (3.70)
HS	859	0.79	2.1	--	--	--
Pd/C	959	0.6	--	--	--	--

Table S2. Quinoline hydrogenation on Pd/HS-NH_2 (5 wt%) with different solvents.

Solvent	Conv. (%)	Sel. (%)	
Cyclohexane	98	>99	aprotic solvent
Toluene	98	>99	
Diethyl ether	99	>99	
Dioxane	82	>99	
Tetrahydrofuran	62	>99	protic solvent
Ethanol	59	>99	
Isopropanol	75	>99	
Water	54	>99	

Table S3. Quinoline hydrogenation catalyzed by different noble mental NPs in literatures.

Catalyst / NPs	Reaction conditions	Sel. (%)	Apparent TOF (h^{-1})	Literatures
Pd/ompg-C_3N_4	1 bar, 50 °C	100	~ 30	Ref. 3
Pd/ Hydroxyapatite	1 bar, 50 °C	97	25	Ref. 4
Pd/Polymer	1 MPa, 80 °C	>99	22.2	Ref. 5
Pd/Polyphenol	2 MPa, 90 °C	100	196.2	Ref. 6
Pd/MgO	4 MPa, 150 °C	>99	300	Ref. 7
Pd/HS-NH_2	3 MPa, 100 °C	>99	5052	This work
Rh/PEG	3 MPa, 100 °C	>99	762	Ref. 8
Rh/ILs	3 MPa, 80 °C	100	95% (Yield)	Ref. 9
Rh/ILs	3 MPa, 50 °C	100	19.2	Ref. 10
Ru-SiO_2	3 MPa, 90 °C	100	30.8	Ref. 11
Ru/Montmorillonite	3 MPa, 100 °C	98.5	156.5	Ref. 12
Ru/Hectorite	3 MPa, 100 °C	100	330	Ref. 13
Ru/Poly(4-vinylpyridine)	3 MPa, 150 °C	92	75	Ref. 14
Au/TiO_2	2 MPa, 140 °C	100	104	Ref. 15
Pt/SiO_2@RF	1 bar, 25 °C	>99	~ 21	Ref. 16

References

1 Y. Yao, X. Zhang, J. Peng and Q. Yang, *Chem. Commun.*, 2015, **51**, 3750.

2 M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. Hratchian, A. Izmaylov, J. Bloino, G. Zheng, J. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. Peralta, F. Ogliaro, M. Bearpark, J. Heyd, E. Brothers, K. Kudin, V. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. Burant, S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. Millam, M. Klene, J. Knox, J. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. Stratmann, O. Yazyev, A. Austin, R. Cammi, C. Pomelli, J. Ochterski, R. Martin, K. Morokuma, G. Zakrzewski, P. Voth, J. Salvador, S. Dannenberg, A. Dapprich, O. Daniels, J. Farkas, V. Foresman, J. Ortiz, J. Cioslowski, D. Fox, Gaussian 09, Revision A. 02; 2009.

3 Y. Gong, P. Zhang, X. Xu, Y. Li, H. Li and Y. Wang, *J. Catal.*, 2013, **297**, 272.

4 N. Hashimoto, Y. Takahashi, T. Hara, S. Shimazu, T. Mitsudome, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Chem. Lett.*, 2010, **39**, 832.

5 M. DellAnna, V. Capodiferro, M. Mali, D. Manno, P. Cotugno, A. Monopoli and P. Mastrorilli, *Appl. Catal. A: Gen.*, 2014, **481**, 89.

6 H. Mao, J. Ma, Y. Liao, S. Zhao and X. Liao, *Catal. Sci. Technol.*, 2013, **3**, 1612.

7 R. Rahi, M. Fang, A. Ahmed and R. Sánchez-Delgado, *Dalton Trans.*, 2012, **41**, 14490.

8 M. Niu, Y. Wang, P. Chen, D. Du, J. Jiang and Z. Jin, *Catal. Sci. Technol.*, 2015, **5**, 4746.

9 A. Karakulina, A. Gopakumar, İ. Akçok, B. Roulier, T. LaGrange, S. Katsyuba, S. Das and P. Dyson, *Angew. Chem. Int. Ed.*, 2016, **55**, 292.

10 H. Jiang and X. Zheng, *Appl. Catal. A: Gen.*, 2015, **499**, 118-123.

11 L. Zhang, X. Wang, Y. Xue, X. Zeng, H. Chen, R. Li and S. Wang, *Catal. Sci. Technol.*, 2014, **4**, 1939.

12 L. Zhou, X. Qi, X. Jiang, Y. Zhou, H. Fu and H. Chen, *J. colloid interface sci.*, 2013, **392**, 201.

13 B. Sun, F. Khan, A. Vallat and G. Süss-Fink, *Appl. Catal. A: Gen.*, 2013, **467**, 310.

14 R. Sánchez-Delgado, N. Machalaba and N. Ng-a-qui, *Catal. Commun.*, 2007, **8**, 2115.

15 D. Ren, L. He, L. Yu, R. Ding, Y. Liu, Y. Cao, H. He and K. Fan, *J. Am. Chem. Soc.*, 2012, **134**, 17592.

16 L. Bai, X. Wang, Q. Chen, Y. Ye, H. Zheng, J. Guo Y. Yin and C. Gao, *Angew. Chem. Int. Ed.*, 2016, **55**, 15656.