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ELECTRONIC SUPPORTING INFORMATION (ESI)

**Pd nanoparticles supported on covalent triazine-based framework
material: An efficient and high chemoselective catalyst for the reduction
of nitroarenes**

Jie Li, Lihong Zhang, Xiaotong Liu, Ningzhao Shang*, Shutao Gao, Cheng Feng, Chun Wang*,

Zhi Wang

College of Science, Hebei Agricultural University, Baoding 071001, China

Experimental section

Cyanuric chloride, melamine, triethylamine, *N,N*-dimethylformamide (DMF), palladium (II) chloride (PdCl_2), and sodium borohydride (NaBH_4 , 96%) were purchased from Aladdin Chemicals Co. Ltd. (Shanghai, China). Formic acid (FA, HCOOH , 88%) and ammonium formate (AF, HCOONH_4 , $\geq 95\%$) were gained from Huaxin Co. Ltd. (Baoding, China). All chemical reagents were used as commercially available and no further purification.

The X-ray diffraction (XRD) patterns of the samples were conducted through a Rigaku D/max 3500 X-ray diffractometer (Dandong, China) using $\text{Cu K}\alpha$ radiation (30 kV, 25 mA) in the range $2\theta = 2^\circ\text{--}80^\circ$. X-ray photoelectron spectroscopy (XPS) spectra were acquired with an ESCA Lab 250 (Thermo) spectrometer using a monochromatic $\text{Al K}\alpha$ source (1486.6 eV). Transmission electron microscopy (TEM) using a JEOL model JEM-2011(HR) (Tokyo, Japan) at 200 kV. The Brunauer–Emmett–Teller (BET) surface areas were determined from the N_2 adsorption at 77 K using V-Sorb 2800P (Jinaipu, China). GC analyses were carried out on a Shimadzu GC-2014-C series gas chromatograph (Shimadzu, Japan) equipped with a flame ionization detector (FID) and a split/splitless injector. All the separations were performed on a HP-5 capillary column (30 m \times 0.25 mm i.d. \times 0.25 μm film thickness) (WondaCap5) was employed to identify all reaction products. The products were characterized by ^1H NMR (300 MHz) spectra.

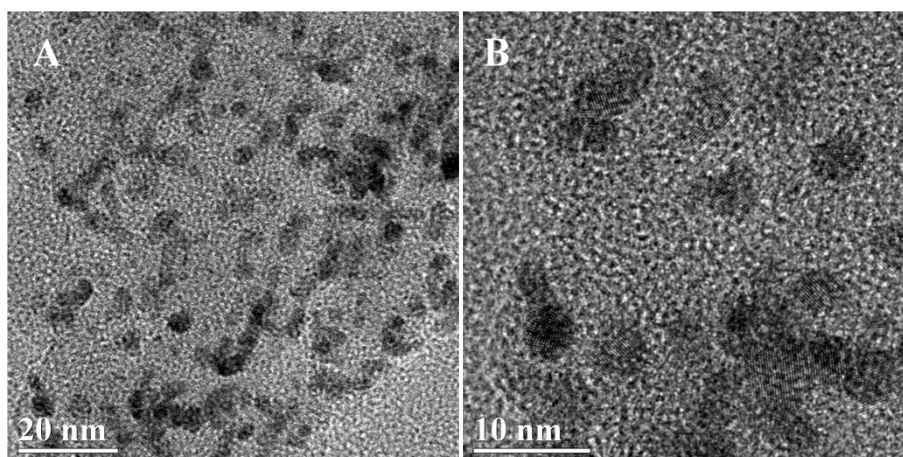


Fig. S1. The TEM images of Pd@CTF (A) and reused of Pd@CTF (B).

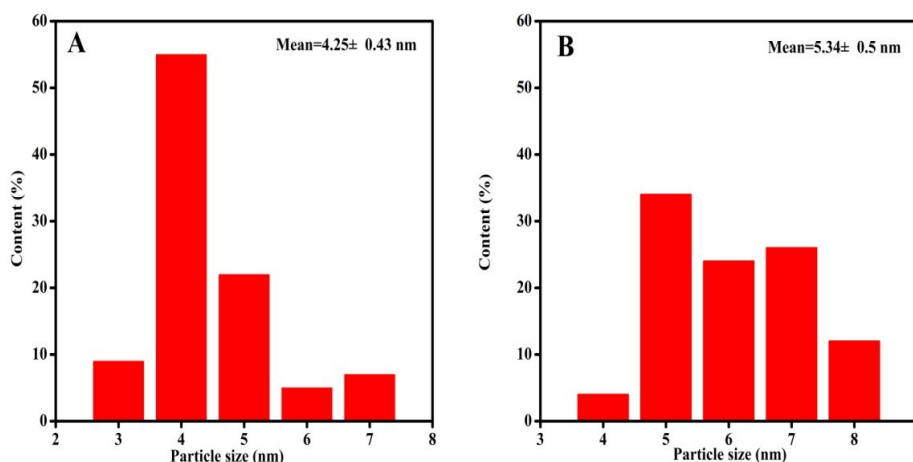


Fig. S2. The particles size of Pd@CTF (A) and reused of Pd@CTF(B).

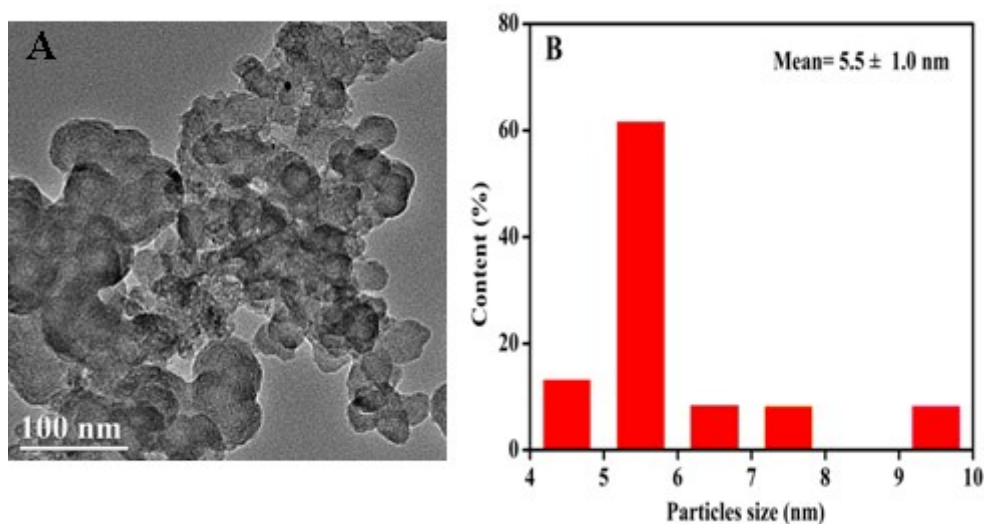


Fig. S3. The TEM image (A) and the particles size (B) of Pd/C.

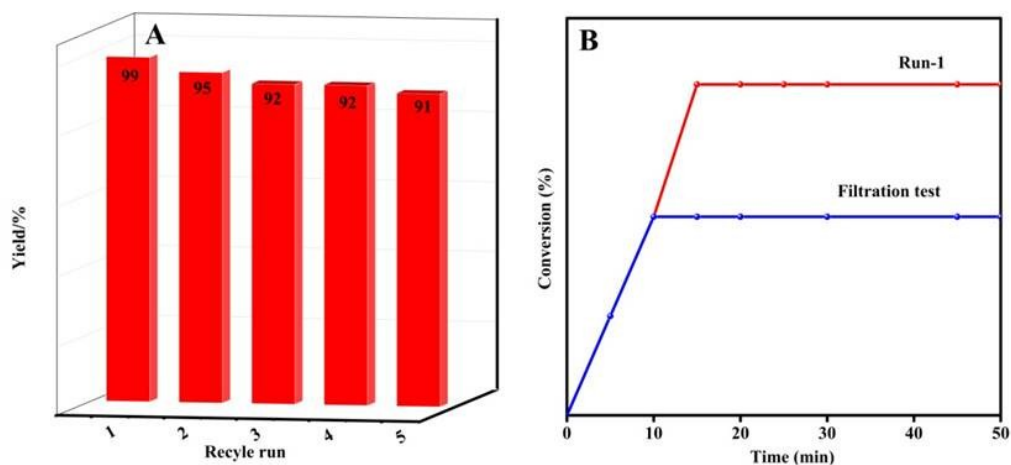


Fig. S4. Durability test (A) and the filtration test for the reduction of nitrobenzene over Pd@CTF (B).

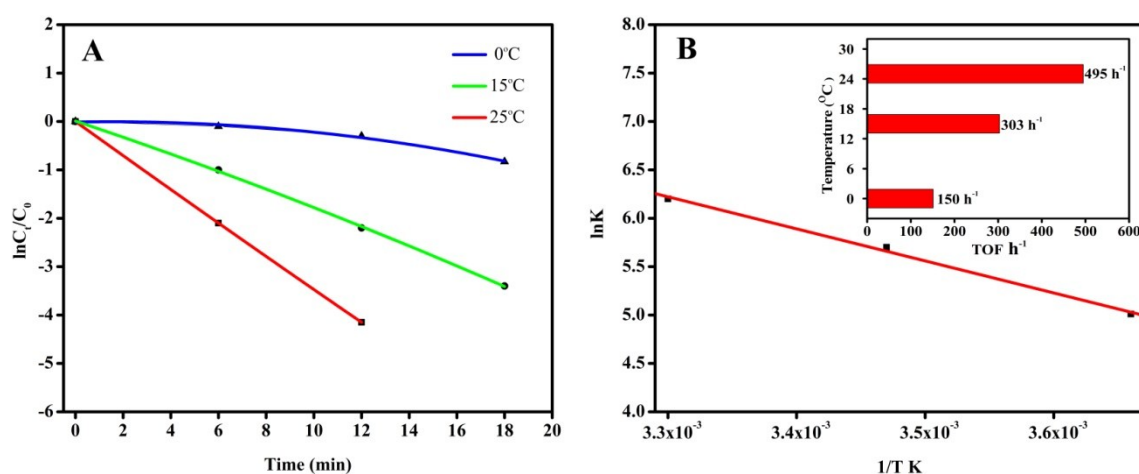


Fig. S5. The reaction rate curve (A) and TOF_{total} data (B) for the catalytic transfer hydrogenation of nitrobenzene at different temperatures (0°C, 15 °C and 25 °C).

Reaction conditions: 1 mmol nitrobenzene, 1.0 mol% Pd, 5 mL EtOH/H₂O (v/v = 4:1), 5 mmol FA,

5 mmol NH₄COOH.

Table S1 Effect of the type of solvent on the catalytic transfer hydrogenation of nitrobenzene

Entry	Solvents	Time (h)	Con. (%)	Sel. (%)	TOF (h ⁻¹)
1	EtOH	0.2	99	99	495
2	EtOH:H ₂ O (v/v = 4:1)	0.2	99	99	495
3	EtOH:H ₂ O (v/v = 3:2)	0.22	99	97	441
4	EtOH:H ₂ O (v/v = 2: 3)	0.25	99	92	368
5	EtOH:H ₂ O (v/v = 1: 4)	0.3	99	89	297
6	H ₂ O	0.3	99	85	283

Reaction conditions: 1 mmol nitrobenzene, 1.0% mmol Pd, 5 mL solvent, 5 mmol FA, 5 mmol NH₄COOH, 25°C, GC analysis using *n*-decane as an internal standard.

Table S2 Various reported catalyst tested for the catalytic transfer hydrogenation into anilines

Entry	Catalyst	Hydrogen source	Temp (°C)	Time (h)	TOF[h ⁻¹] ^[a]	Ref
1	Au/rutile	HCOOH	60	0.67-4	25-149	[1]
2	Fe(BF ₄) ₂ ·6H ₂ O/PP ₃	HCOOH	40	1	100	[2]
3	[Mo ₃ S ₄ H ₃ (dmpe) ₃]BPh ₄ ^[a]	HCOOH-Et ₃ N	70	18	0.54-1.85	[3]
4	Fe-MMIO ^[c]	HCOOH	70	0.67-1	20-25	[4]
5	γ-Fe ₂ O ₃ @HAP-Pd ^[b]	HCOONH ₄	60	3	35-30	[5]
6	Fe ₂ O ₃ /NGr@C	HCOOH-Et ₃ N	120	20-24	0.74-0.95	[6]
7	Pd@CTF	HCOOH-NH ₄ COOH	25	0.2-2.5	36.4-495	This work

[a] dmpe = 1,2-(bis)dimethylphosphinoethane.

[b] HAP = hydroxyapatite.

[c] MMIO = micro-mesoporous iron oxide.

The spectroscopic data of the products.

1. Aniline (Table 2, Entry 1), ¹H-NMR (300 MHz, CDCl₃): δ 3.70 (br, 1H), 6.77 (d, 2H), 6.87 (t, 1H), 7.30 (d, 2H).
2. 2-Tuluidine (Table 2, Entry 2), ¹H-NMR (300 MHz, CDCl₃): δ 7.24 (t, 2H), 6.92 (t, 1H), 6.80 (d, 1H), 3.68 (br, 2H), 2.30 (s, 3H).

3. 4-Tuluidine (Table 2, Entry 3), $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.05 (d, 2H), 6.67 (d, 2H), 3.54 (br, 2H), 2.31 (s, 3H).
4. 2-Aminophenol (Table 2, Entry 4), $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 4.49 (bs, 2H), 6.36-6.42(m, 1H), 6.51-6.65 (m, 3H), 8.95 (bs, 1H).
5. 4-Aminophenol (Table 2, Entry 5), $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 4.00 (bs, 2H), 6.31-6.39 (m, 4H), 8.95 (bs, 1H).
6. 4-Aminophenyl-methano (Table 2, Entry 6), $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.13 (d, 2H), 6.65 (d, 2H), 4.50 (s, 2H), 3.08 (br, 2H).
7. 1,4-Phenylenediamine (Table 2, Entry 7), $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 6.57 (s, 4H), 3.20 (br, 4H).
8. 4-Anisidine (Table 2, Entry 8), $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 6.76 (d, 2H), 6.65 (d, 2H), 3.74 (s, 3H), 3.32 (br, 2H).
9. 4-Aminotenzaldehyde (Table 2, Entry 9), $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 2.50 (s, 3H), 4.16 (brs. 2H), 6.63 (d, 2H), 7.79 (d, 2H);
10. 4- Amino-acetophenone (Table 2, Entry 10), $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.84 (m, 2H), 6.68 (m, 2H), 4.11 (bs, 3H);
11. 2-Aminoacetophenone (Table 2, Entry 11), $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.04 (m, 2H), 6.5 (m, 2H), 4.23 (bs, 3H);
12. 3-Aminoacetophenone (Table 2, Entry 12), $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.34 (m, 2H), 6.27(m, 2H), 4.3(bs, 3H);
13. 1-Aminonaphthalene (Table 2, Entry 13), $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 4.01(br, 2H), 6.82 (d, 1H), 7.33 (m, 2H), 7.48 (m, 2H), 7.84 (m, 2H);
14. 4-Aminobenzonitrile (Table 2, Entry 14), $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 3.84(s, 3H), 4.17(br, 2H), 6.61(d, 2H), 7.82(d, 2H);
15. 2-Methyl-2-aminopropane (Table 2, Entry 15), $^1\text{H-NMR}$ (CDCl_3): δ 1.53 (d, 6H), 1.62 (s, 3H), 1.38 (m, 2H).

References

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