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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\(_4\), ≥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 though a Rigaku D/max 3500 X-ray diffractometer (Dandong, China) using Cu K\( \alpha \) radiation (30 kV, 25 mA) in the range 2\( \theta \) = 2°–80°. X-ray photoelectron spectroscopy (XPS) spectra were acquired with an ESCA Lab 250 (Thermo) spectrometer using a monochromatic 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 \( \times \) 0.25mm i.d. \( \times \) 0.25 \( \mu \)m film thickness) (WondaCap5) was employed to identify all reaction products. The products were characterized by \(^1\)H NMR (300 MHz) spectra.

![Fig. S1. The TEM images of Pd@CTF (A) and rused of Pd@CTF (B).](image1)

![Fig. S2. The particles size of Pd@CTF (A) and rused of Pd@CTF(B).](image2)
**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/H_2O (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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvents</th>
<th>Time (h)</th>
<th>Con. (%)</th>
<th>Sel. (%)</th>
<th>TOF (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EtOH</td>
<td>0.2</td>
<td>99</td>
<td>99</td>
<td>495</td>
</tr>
<tr>
<td>2</td>
<td>EtOH: H₂O (v/v = 4:1)</td>
<td>0.2</td>
<td>99</td>
<td>99</td>
<td>495</td>
</tr>
<tr>
<td>3</td>
<td>EtOH: H₂O (v/v = 3:2)</td>
<td>0.22</td>
<td>99</td>
<td>97</td>
<td>441</td>
</tr>
<tr>
<td>4</td>
<td>EtOH: H₂O (v/v = 2:3)</td>
<td>0.25</td>
<td>99</td>
<td>92</td>
<td>368</td>
</tr>
<tr>
<td>5</td>
<td>EtOH: H₂O (v/v = 1:4)</td>
<td>0.3</td>
<td>99</td>
<td>89</td>
<td>297</td>
</tr>
<tr>
<td>6</td>
<td>H₂O</td>
<td>0.3</td>
<td>99</td>
<td>85</td>
<td>283</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Hydrogen source</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>TOF[h⁻¹][a]</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Au/rutile</td>
<td>HCOOH</td>
<td>60</td>
<td>0.67-4</td>
<td>25-149</td>
<td>[1]</td>
</tr>
<tr>
<td>2</td>
<td>Fe(BF₄)₂·6H₂O/PP₃</td>
<td>HCOOH</td>
<td>40</td>
<td>1</td>
<td>100</td>
<td>[2]</td>
</tr>
<tr>
<td>3</td>
<td>[Mo₃S₄H₃(dmpe)₃]BPh₄[a]</td>
<td>HCOOH-Et₃N</td>
<td>70</td>
<td>18</td>
<td>0.54-1.85</td>
<td>[3]</td>
</tr>
<tr>
<td>4</td>
<td>Fe-MMIO[c]</td>
<td>HCOOH</td>
<td>70</td>
<td>0.67-1</td>
<td>20-25</td>
<td>[4]</td>
</tr>
<tr>
<td>5</td>
<td>γ-Fe₂O₃@HAP-Pd[b]</td>
<td>HCOONH₄</td>
<td>60</td>
<td>3</td>
<td>35-30</td>
<td>[5]</td>
</tr>
<tr>
<td>6</td>
<td>Fe₂O₃/NGr@C</td>
<td>HCOOH-Et₃N</td>
<td>120</td>
<td>20-24</td>
<td>0.74-0.95</td>
<td>[6]</td>
</tr>
<tr>
<td>7</td>
<td>Pd@CTF</td>
<td>HCOOH-NH₄COOH</td>
<td>25</td>
<td>0.2-2.5</td>
<td>36.4-495</td>
<td>This work</td>
</tr>
</tbody>
</table>

[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), $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 7.05 (d, 2H), 6.67 (d, 2H), 3.54 (br, 2H), 2.31 (s, 3H).

4. 2-Aminophenol (Table 2, Entry 4), $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 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), $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 4.00 (bs, 2H), 6.31-6.39 (m, 4H), 8.95 (bs, 1H).

6. 4-Aminophenyl-methano (Table 2, Entry 6), $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 7.13 (d, 2H), 6.65 (d, 2H), 4.50 (s, 2H), 3.08 (br, 2H).

7. 1,4-Phenylenediamine (Table 2, Entry 7), $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 6.57 (s, 4H), 3.20 (br, 4H).

8. 4-Anisidine (Table 2, Entry 8), $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 6.76 (d, 2H), 6.65 (d, 2H), 3.74 (s, 3H), 3.32 (br, 2H).

9. 4-Aminotenzaldehyde (Table 2, Entry 9), $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 2.50 (s, 3H), 4.16 (bs, 2H), 6.63 (d, 2H), 7.79 (d, 2H).

10. 4-Amino-acetophenone (Table 2, Entry 10), $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 7.84 (m, 2H), 6.68 (m, 2H), 4.11 (bs, 3H);

11. 2-Aminoacetophenone (Table 2, Entry 11), $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 7.04 (m, 2H), 6.5 (m, 2H), 4.23 (bs, 3H);

12. 3-Aminoacetophenone (Table 2, Entry 12), $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 7.34 (m, 2H), 6.27 (m, 2H), 4.3 (bs, 3H);

13. 1-Aminonaphthalene (Table 2, Entry 13), $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 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), $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 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), $^1$H-NMR (CDCl$_3$): $\delta$ 1.53 (d, 6H), 1.62 (s, 3H), 1.38 (m, 2H).

References


