Supporting Information

Metallo-supramolecular polymers engineered porous carbon frameworks encapsulated stable ultra-small nanoparticles: a general approach to construct highly dispersed catalysts

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Table of contents

1. General information of characterization.................................................................S2

2. Materials characterization....................................................................................S3-S8

3. Comparison of catalyst activity.............................................................................S9

4. GC-MS data of Anilines.....................................................................................S9-S12

References..............................................................................................................S13-S14
1. **General information of characterization**

The materials morphology was observed by the JEOL SU-8010 scanning electron microscopy (SEM) and JEM-2100F high resolution transmission electron microscopy (HR-TEM). The scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDS) are accessories of the HR-TEM apparatus. Fourier transform infrared (FT-IR) spectra were obtained by a Bruker IFS28 spectrometer in the region of 4000–500 cm\(^{-1}\). The solid-state nuclear magnetic resonance (NMR) instrument was JEOL JNMECZ600R. The X-ray diffraction (XRD) experiments were recorded on a Rigaku corporation Smart-Lab, diffractometer using Cu K\(\alpha\) radiation (\(\lambda = 0.1541\) nm). X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI Quantera SXM spectrometer, ULVAC-PHI, and the binding energy determination was based on the C 1s at 284.8 eV with an experimental error of ±0.2 eV. Nitrogen adsorption/desorption measurements were conducted with a Tristar II 3020 volumetric adsorption analyzer at -196 °C. Thermogravimetric analysis (TGA) was carried with a STA449F3 instrument under air atmosphere. Raman spectra were recorded with a Horiba HR-800 spectrometer equipped with a charge coupled device detector cooled by liquid nitrogen. The inductively coupled plasma mass spectrometry (ICP-MS) is PerkinElmer ELAN DRC-e. The AFM was Cypher S (Asylum Research). The detailed reaction procedure was further detected by the UV-visible spectrophotometer (UV-6100 double-beam spectrophotometer). This reaction system was also applied to the hydrogenation of varieties of nitroaromatics with different functional groups. All reactions were monitored by TLC (petroleum ether/ethyl acetate), HPLC (Waters, Kromasil 5mm C18 column) and detected by GC-MS (Bruker 450GC-320MS).
2. Materials characterization

Figure S1. Pathway for the fabrication of metallo-supramolecular polymers.

Figure S2. TGA curves of the metallo-supramolecular polymer precursor: (a) Fe, (b) Co, (c) Ni, (d) Mo, (e) Ru, (f) Rh, (g) Pd, (h) Pt.
Figure S3. HR-TEM images of Pd@PCF that the polymer precursors annealed at (a) 600 °C and (b) 800 °C.

Figure S4. EDS spectrum of Pd@PCF.

Figure S5. (a) The solid-state $^{13}$C NMR of Pd@PCF.
Figure S6. (a) AFM images of the Pd@PCF nanocatalysts, (b-c) the thickness of the PCF.

Figure S7. The XRD pattern of Pd@PCF annealed at different temperature.

Figure S8. (a) XPS survey spectrum of the Pd@PCF obtained from different temperature; (b) XPS spectrum of the Pd 3d region of Pd@PCF.
Figure S9. Nitrogen adsorption/desorption isotherms of the Pd@PCF nanocatalysts.

Figure S10. Raman spectra of the Pd@PCF nanocatalysts.

Figure S11. TGA curves of the Pd@PCF nanocatalysts (air atmosphere).
Figure S12. DSC curves of the Pd@PCF nanocatalysts (air atmosphere)

Figure S13. STEM images of M@PCF: (a) Fe, (b) Co, (c) Ni, (d) Mo, (e) Ru, (f) Rh, (g) Pd, (h) Pt

Figure S14. XPS survey spectroscopy of M@PCF: (a) Fe, (b) Co, (c) Ni, (d) Mo, (e) Ru, (f) Rh, (g) Pd, (h) Pt
Figure S15. TEM image of ultra-small Pd nanoparticles as Prasad reported.

Figure S16. (a-b) HRTEM, (c) EDS images of Pd@PCF after used for 10 cycles.
3. Comparison of catalyst activity

Table S1. Comparison of the ability of various noble metal-based catalysts for catalyzing hydrogenation of nitroarenes.

<table>
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<th>Entry</th>
<th>Catalyst</th>
<th>Reactant</th>
<th>Time (min)</th>
<th>Conv. (%)</th>
<th>TOF (h⁻¹)</th>
<th>Ref.</th>
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<td>Pd NP/CNT</td>
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<td>7</td>
<td>&gt;99</td>
<td>1080</td>
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<td>&gt;99</td>
<td>7440</td>
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<td>&gt;99</td>
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4. GC-MS Data of Anilines:

4-Aminophenol (Table 2, entry 1):

\[
\text{OH} \\
\text{NH}_2
\]

GC-MS: \( m/z \) (\%) 109 (100) [M]+, 80 (50), 52 (14).\[19\]

4-Chlorobenzenamine (Table 2, entry 2):

\[
\text{Cl} \\
\text{NH}_2
\]

GC-MS: \( m/z \) (\%) 127 (100) [M]+, 92 (13), 65 (21).\[20\]

2-Chloroaniline (Table 2, entry 3):

\[
\text{Cl}
\]

GC-MS: \( m/z \) (\%) 127 (100) [M]+, 92 (14), 65 (17).\[21\]

3-Bromoanilines (Table 2, entry 4)

\[
\text{Br}
\]

GC-MS: \( m/z \) (\%) 173 (100) [M]+, 92 (91), 65 (85).\[21\]

4-Fluoroaniline (Table 2, entry 5)

\[
\text{F}
\]

GC-MS: \( m/z \) (\%) 111 (100) [M]+, 84 (43), 57 (11).\[21\]

2-Hydroxy-5-chloro-aniline (Table 2, entry 6):

\[
\text{Cl} \\
\text{OH} \\
\text{NH}_2
\]

GC-MS: \( m/z \) (\%) 143 (100) [M]+, 114 (14), 80 (31), 51 (10).\[22\]

2,6-Dichloro-4-aminophenol (Table 2, entry 7):
GC-MS: m/z (%) 177 (100) [M]+, 113 (87), 78 (60), 52 (16). [22]

4-Toluidine (Table 2, entry 8):

GC-MS: m/z (%) 106 (100) [M]+, 77 (12). Physical and spectral data were consistent with those previously reported. [23]

(3-Aminophenyl)-methanol (Table 2, entry 9):

GC-MS: m/z (%) 123 (100) [M]+, 94 (74), 77 (30), 65 (13), 39 (8). [24]

3-Aminostyrene (Table 2, entry 10):

GC-MS: m/z (%) 119 (100) [M]+, 91 (28), 89 (5), 65 (13). [25]

Methyl 4-aminobenzoate (Table 2, entry 11):

GC-MS: m/z (%) 151 (54) [M]+, 120 (100), 92 (26), 65 (20). [26]

4-Methoxyaniline (Table 2, entry 12):

GC-MS: m/z (%) 108 (100) [M]+, 80 (36), 53 (14). [26]

4-Aminobenzamide (Table 2, entry 13):
1,4-Benzene diamine (Table 2, entry 14):

![1,4-Benzene diamine](image)

GC-MS: m/z (%): 136 (73) [M]+, 120 (100), 92 (34), 65 (27), 39 (8).[23]

5-(Aminophenyl)-1,3-dioxolane (Table 2, entry 15):

![5-(Aminophenyl)-1,3-dioxolane](image)

GC-MS: m/z (%): 165 (99) [M]+, 120 (52), 93 (100), 65 (26).[23]

6-Amino-1H-benzimidazole (Table 2, entry 16):

![6-Amino-1H-benzimidazole](image)

GC-MS: m/z (%): 133 (100) [M]+, 106 (15), 78 (8), 52 (12).[21]

4-Aminodiphenyl ether (Table 2, entry 17):

![4-Aminodiphenyl ether](image)

GC-MS: m/z (%): 185 (100) [M]+, 156 (17), 108 (74), 80 (25), 51 (13).[27]

4-(4-Chlorophenoxy)benzenamine (Table 2, entry 18):

![4-(4-Chlorophenoxy)benzenamine](image)

GC-MS: m/z (%): 219 (72) [M]+, 156 (13), 108 (100), 80 (30).[24]
GC-MS: m/z (\%) 177 (51) [M]+, 135 (100), 120 (30), 92 (10) 65 (11).\cite{27}

4-(Benzyl oxy)benzenamine (Table 2, entry 20):

GC-MS: m/z (\%) 199 (15) [M]+, 108 (100), 91 (29), 80 (14), 53 (5).\cite{28}

References


[22]. AIST: Integrated Spectral Database System of Organic Compounds. (Data were obtained from the National Institute of Advanced Industrial Science and Technology (Japan))


