Supporting Information

Metal−Organic Framework Encapsulated Pd Nanoparticles: towards Advanced Heterogeneous Catalysts

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Materials and Methods

Figs. S1 to S6

Table S1
Experimental

1. Catalysts preparation

All chemicals were purchased from commercial sources and used without further treatments.

1.1 Synthesis of [(5,5’-dimethoxylcarboxyl-2,2’-bipyridine-)palladium(II)] dichloride (Me₂L).

A mixture of PdCl₂(CH₃CN)₂ (130 mg, 0.5 mmol) and dimethyl (2,2’-bipyridine)-5,5’-dibenzoate (Me₂bpydc) (136 mg, 0.5 mmol) in 8 mL of CH₃CN was stirred at 65 °C for 24 hours. The resulting yellow solid was collected by filtration and was washed with CH₃CN and then was heated at 100 °C for 12 h under vacuum.

\[
\text{Me}_2\text{bpydc} + \text{PdCl}_2(\text{CH}_3\text{CN})_2 \rightarrow \text{PdCl}_2(\text{Me}_2\text{bpydc}) \quad \text{(Me}_2\text{L)}
\]

1.2 Synthesis of [(5,5’-dicarboxy-2,2’-bipyridine-)palladium(II)] dichloride (H₂L).

A solution of [(5,5’-dimethoxylcarboxyl-2,2’-bipyridine-)palladium(II)] dichloride (Me₂L) (120 mg, 0.27 mmol) in tetrahydrofuran (THF) (10 mL), ethanol (10 mL), and 3 M aqueous NaOH (10 mL) was stirred at 70 °C for 5 hours. The solution was cooled to room temperature, acidified to a pH of 1. A yellow solid was obtained, and washed with H₂O and methanol to afford the product. \(^{1}\text{H NMR (400 MHz, D}_2\text{O) } \delta = 8.79 \text{ (s, 2H), 8.61 \text{ (d, J=8.4 Hz, 2H), 8.37 \text{ (d, J=8.4 Hz, 2H).}}\)

\[
\text{Me}_2\text{L} \rightarrow \text{H}_2\text{L}
\]
1.3 Synthesis of Pd(II)-in-Uio-67

For the synthesis of 1.0% Pd(II)-in-Uio-67: ZrCl$_4$ (70.0 mg), H$_2$L (4.2 mg) and H$_2$bpdc (H$_2$bpdc, para-biphenyldicarboxylic acid) (70.24 mg) were dispersed in DMF (10 mL), sealed in a 25 mL tube at 100 °C for 36 hours. The produced powders were isolated by centrifugation and dried at ambient temperature. Subsequently, the as-synthesized sample was soaked in chloroform for three 18 hours periods at room temperature to remove DMF and ligand precursors, then filtered off and dried under vacuum at room temperature for 24 h. Finally, the sample was heated under vacuum at 150 °C overnight to remove the solvents. Different Pd contents could be loaded on Uio-67 by adjusting the ratio of H$_2$L and H$_2$bpdc.

1.4 Synthesis of Pd$^0$-in-Uio-67

The Pd(II)-in-Uio-67 was treated in the stream of H$_2$ at 250 °C for 4 h to yield Pd$^0$-in-Uio-67.

1.5 Synthesis of Pd/C

Pd/C catalyst was prepared via a simple impregnation method. Typically, 200 mg of activated carbon was dispersed in 10 mL of DMF and was stirred for 0.5 h at room temperature. 0.3 mL Pd(NO$_3$)$_2$ solution that was pre-prepared by dissolving 10...
mg Pd(NO$_3$)$_2$·2H$_2$O in 2 mL DMF was added dropwise to the above solution under vigorous agitation for about 10 min. The flask containing the slurry was subjected to ultrasounication for 20 min and was then magnetically agitated at room temperature for 24 h. The impregnated carbon sample was washed with DMF till the filtrate became colorless and then was slowly dried under air at room temperature for 24 h to obtain Pd$^{II}$/C. The as-synthesized sample was further dried at 150 °C for 8 h, followed by treating in a stream of H$_2$ at 200 °C for 2 h to yield Pd/C. The Pd loading on the sample was 0.5 wt% based on Atomic Absorption Spectroscopy (AAS) analysis.

2. Catalyst characterization and catalytic reactions

2.1 Characterization

The BET surface area measurements were performed with N$_2$ adsorption/desorption isotherms at 77 K on a Micromeritics ASAP 2020M instrument. Before the analysis, the samples were evacuated at 150 °C for 12 h.

Powder X-ray diffraction patterns of the samples were recorded on a Rigaku diffractometer (D/MAX-IIIA, 3 kW) using Cu K$\alpha$ radiation (40 kV, 30 mA, $\lambda = 0.1543$ nm). The size and morphology of Pd(II) doped UiO-67 were investigated by using a transmission electron microscope (TEM, JEOL, JEM-2010HR) with EDX analysis (Oxford INCA EDS) operated at 300 kV. The palladium contents of the samples were determined quantitatively by AAS on a HITACHI Z-2300 instrument.

2.2 Catalytic reactions
Typical procedures for olefin hydrogenation: olefin (0.1 mmol) and supported palladium catalyst (1 mol%) were added to 2 mL of THF. The reaction mixture was stirred at room temperature under 1 atm hydrogen atmosphere for 1h. Upon reaction completion, the catalyst particles were removed from the solution by filtration and washed with THF. The liquid phase was subsequently analyzed by GC/MS (Shimadzu GCMS-QP5050A equipped with a 0.25 mm × 30 m DB-WAX capillary column).

Typical procedures for aerobic oxidation of alcohol: alcohol (1 mmol) and supported palladium catalyst (1 mol%) were added to 10 mL of toluene. The reaction mixture was stirred at the desired temperature under air atmosphere. Upon reaction completion, the catalyst particles were removed from the solution by filtration and washed with toluene. The liquid phase was subsequently analyzed by GC/MS (Shimadzu GCMS-QP5050A equipped with a 0.25 mm × 30 m DB-WAX capillary column).

Typical procedures for the reduction of nitrobenzene: 1.0% Pd⁰-in-Uio-67 (1 mol%) and nitrobenzene (0.1 mmol) in THF (3 mL) under 1 atm hydrogen atmosphere was stirred at room temperature for 3 h. Upon reaction completion, the catalyst particles were removed from the solution by filtration and washed with THF. The liquid phase was subsequently analyzed by GC/MS (Shimadzu GCMS-QP5050A equipped with a 0.25 mm × 30 m DB-WAX capillary column).

For the recyclability tests, the reactions were performed under the same reaction conditions as described above, except using the recovered catalyst. Each time, the
catalyst was isolated from the reaction solution at the end of the reaction, washed with toluene, and then heated at 150 °C under vacuum.
**Figure S1.** Powder XRD patterns of UiO-67 samples: (a) UiO-67; (b) 0.3% Pd\(^0\)-in-UiO-67; (c) 0.6% Pd\(^0\)-in-UiO-67; (d) 1.0% Pd\(^0\)-in-UiO-67; (e) 2.0% Pd\(^0\)-in-UiO-67; (f) 0.6% Pd\(^0\)/UiO-67 prepared by impregnation method; (g) 1.0% Pd\(^0\)-in-UiO-67 after five runs.
Figure S2. Nitrogen adsorption isotherms at 77 K of the as-synthesized UiO-67 (*), 0.3% Pd$^{0}$-in-UiO-67 (■), 0.6% Pd$^{0}$-in-UiO-67 (▲), 1.0% Pd$^{0}$-in-UiO-67 (●), 2.0% Pd$^{0}$-in-UiO-67 (◆), and 0.6% Pd$^{0}$/UiO-67 (○).
<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{BET}}$ (m$^2$ g$^{-1}$)</th>
<th>$S_{\text{Langmuir}}$ (m$^2$ g$^{-1}$)</th>
<th>$V_{\text{pore}}$ (cm$^3$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UiO-67</td>
<td>2228</td>
<td>2507</td>
<td>0.89</td>
</tr>
<tr>
<td>0.3% Pd$^0$-in-UiO-67</td>
<td>1994</td>
<td>2216</td>
<td>0.79</td>
</tr>
<tr>
<td>0.6% Pd$^0$-in-UiO-67</td>
<td>1963</td>
<td>2152</td>
<td>0.78</td>
</tr>
<tr>
<td>1.0% Pd$^0$-in-UiO-67</td>
<td>1919</td>
<td>2135</td>
<td>0.76</td>
</tr>
<tr>
<td>2.0% Pd$^0$-in-UiO-67</td>
<td>1909</td>
<td>2122</td>
<td>0.75</td>
</tr>
<tr>
<td>0.6% Pd$^0$/UiO-67</td>
<td>1487</td>
<td>1676</td>
<td>0.59</td>
</tr>
</tbody>
</table>
Figure S3. TEM of 1.0% Pd\(^0\)/UiO-67 and corresponding size distribution of Pd nanoparticles.
Figure S4. TEM image of 0.6% Pd⁰/UiO-67 and corresponding size distribution of Pd nanoparticles.
**Figure S5.** TEM image of 0.5% Pd/C and corresponding size distribution of Pd nanoparticles.
**Figure S6.** (a) TEM of 1.0% Pd⁰-in-Uio-67 after ten cycles, (b) corresponding size distribution of Pd nanoparticles.