Palladium Nanoparticles in Polymers: Catalyst for Alkene Hydrogenation, Carbon–Carbon Cross-Coupling Reactions, and Aerobic Alcohol Oxidation

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Abstract: A new recyclable palladium catalyst was synthesized by a simple procedure from readily available reagents, which is composed of palladium nanoparticles dispersed in an organic polymer. This catalyst is robust, and highly active in many organic transformations including alkene and alkyne hydrogenation, carbon–carbon cross-coupling reactions, and aerobic alcohol oxidation.

Key words: palladium, heterogeneous, hydrogenation, oxidations, cross-coupling, polymer

Palladium catalysts are versatile and used in many organic transformations.1 Homogeneous palladium catalysts are often used, but the difficulty in separation and reuse hinders practical applications. Heterogeneous palladium catalysts have been devised mainly by immobilizing molecular palladium species onto inorganic supports or organic polymers.2 Palladium nanoparticles,3 colloidal palladium species,4 and polymer-incarcerated palladiums5 have been also reported as recyclable heterogeneous catalysts. However, they often suffer from low reactivity, degradation, palladium leaching, and difficult synthetic procedures. As a noticeable example of the recyclable palladium catalyst, Kobayashi et al. have developed the ‘polymer-incarcerated palladium’ (PI Pd) catalysts and have applied them to various organic transformations. An essential step for the synthesis of PI Pd catalysts is the formation of microcapsules consisting of Pd(PPh3)4 and an epoxide-containing copolymer which is then cross-linked thermally. Meanwhile, our group has developed a simple but novel synthetic method for recyclable metal-nanoparticle catalysts.6 A novel idea of our method is the generation of regular metal nanoparticles in a solution of inorganic gel precursors before gelation. This method provides heterogeneous catalysts consisting of well-dispersed metal nanoparticles and solid inorganic supports. Herein, we describe the synthesis of a polymer-supported palladium catalyst, which employs organic monomers instead of the inorganic gel precursors. The polymer-supported catalyst is robust, recyclable, and highly active in many organic transformations including alkene hydrogenation, carbon–carbon cross-coupling reactions, and aerobic alcohol oxidation.

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The catalyst 1 was tested on the hydrogenation of trans-stilbene in THF, EtOAc, chloroform, diethyl ether, and DMF (Table 1). The reaction in THF was fastest and that in DMF was most slow. The recyclability of 1 for the hydrogenation was very high; it could be recovered by simple filtration in the air and was reused 16 times with showing practically same reactivity as that in the first use. Notably, the catalyst recovered from the 15th use was kept in the air for 40 days (Table 2).12

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>TOF (h⁻¹)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>THF</td>
<td>270</td>
</tr>
<tr>
<td>2</td>
<td>EtOAc</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>CHCl₃</td>
<td>150</td>
</tr>
<tr>
<td>4</td>
<td>Et₂O</td>
<td>150</td>
</tr>
<tr>
<td>5</td>
<td>DMF</td>
<td>70</td>
</tr>
</tbody>
</table>

a The hydrogenation was performed on 1.00 mmol of trans-stilbene dissolved in 5 mL of solvent with 1 (0.5 mol% of Pd) at 25 °C for 0.5 h under 1 atm H₂.
b The turnover frequency (TOF) is defined as the turnover number per unit time per palladium atom in the catalyst.

The hydrogenation of various alkenes and alkynes were carried out to see the scope of the activity of 1 (Table 3). The use of only 0.5 mol% of Pd in 1 completed the hydrogenation of alkenes, 1,3-dienes, alkenes, α,β-unsaturated carbonyl compounds in 1.5 hours at room temperature under 1 atm H₂. In comparison to the previous PI Pd catalyst, the activity of which is comparable to that of commercial 5% Pd/C,5f1 showed about 10 times higher activity. Meanwhile, in the hydrogenations of benzalacetone and trans-chalcone, the C=O double bonds were also hydrogenated and corresponding alcohols were produced in 3% and 16%, respectively. Sterically hindered alkenes such as trisubstituted cyclic alkenes, oleic acid, and cholesterol required much longer reaction time (entries 9–12). Particularly, cholesterol was hydrogenated in only 11% even after 24 hours.

The catalyst was also active in various carbon–carbon cross-coupling reactions such as the Suzuki–Miyaura, the Heck–Mizoroki, the Sonogashira, and allylation reactions (Scheme 2). In general, the activity of 1 was higher than those of palladium nanospheres,5f palladium clusters,3h and PI Pd catalyst. For example, in the case of PI Pd cata-

**Table 1** Catalytic Hydrogenation of trans-Stilbenea

<table>
<thead>
<tr>
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<th>Solvent</th>
<th>TOF (h⁻¹)b</th>
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<tbody>
<tr>
<td>1</td>
<td>THF</td>
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<td>70</td>
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</tbody>
</table>

a The hydrogenation was performed on 1.00 mmol of trans-stilbene dissolved in 5 mL of solvent with 1 (0.5 mol% of Pd) at 25 °C for 0.5 h under 1 atm H₂.
b The turnover frequency (TOF) is defined as the turnover number per unit time per palladium atom in the catalyst.

**Table 2** Recycling of 1 for the Hydrogenation of trans-Stilbenea

<table>
<thead>
<tr>
<th>Cycle</th>
<th>1b</th>
<th>2–12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (%)c</td>
<td>100</td>
<td>100</td>
<td>99</td>
<td>99</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

a The hydrogenation was performed on 1.00 mmol of substrate dissolved in 5 mL of THF with 1 (0.5 mol% of Pd) at 25 °C for 1 h under 1 atm H₂.
b After 30 min, 1,2-diphenylethane was produced in 68%.
c Isolated yield.

der, the allylation reactions have been carried out with 5 mol% of Pd to give results comparable to those given by 1 mol% of Pd in 1.5f In contrast to the conditions for the hydrogenation, the activity of deteriorated 1 in reuse for the carbon–carbon cross-coupling reactions was significantly lower than that of the first use. In the Suzuki–Miyaura reaction, the activity in the third reuse was only 38% of the original activity due to palladium leaching or palladium nanoparticle aggregation. Particularly, palladium leaching was suggested in the allylation reactions; as in the case of the PI Pd catalyst triphenylphosphine was essential and the reaction did not proceed without the ligand.5f

The activity of 1 for aerobic alcohol oxidation was also tested (Table 4).5c Benzyl alcohol in toluene was oxidized to benzaldehyde quantitatively in 9 hours with 0.5 mol% of Pd at 80 °C under atmospheric air. The catalyst was recovered by simple filtration and reusable three times. However, the activity was lowered dramatically in the fourth reuse; only 35% of the original activity was shown. The oxidations of secondary alcohols and primary aliphatic alcohols were much slower than that of benzyl alcohol. Particularly, aliphatic alcohols were almost inert under the conditions employed in the oxidation of benzyl alcohol.
Scheme 2  Carbon–carbon cross-coupling reactions

Table 4  Aerobic Alcohol Oxidation

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>9</td>
<td>99</td>
</tr>
<tr>
<td>2 (1st reuse)</td>
<td></td>
<td></td>
<td>9</td>
<td>98</td>
</tr>
<tr>
<td>3 (2nd reuse)</td>
<td></td>
<td></td>
<td>9</td>
<td>98</td>
</tr>
<tr>
<td>4 (3rd reuse)</td>
<td></td>
<td></td>
<td>9</td>
<td>82</td>
</tr>
<tr>
<td>5 (4th reuse)</td>
<td></td>
<td></td>
<td>9</td>
<td>35</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td>24</td>
<td>6</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td>24</td>
<td>trace</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td>24</td>
<td>trace</td>
</tr>
</tbody>
</table>

* The oxidation of alcohols was performed on 1.00 mmol of substrate dissolved in 5 mL of toluene with 1 (0.5 mol% of Pd) at 80 °C under atmospheric air.

b Determined by GC.
In summary, we have developed a simple method for preparing a polymer-supported palladium catalyst from readily available reagents, and demonstrated their high catalytic activities in the hydrogenations of alkenes and alkynes, carbon–carbon cross-coupling reactions, and aerobic alcohol oxidation.

Catalyst 1

Pd(PPh$_3$)$_4$ (99.4 mg, 0.086 mmol), butan-1-ol (64.0 mg, 0.864 mmol), styrene (809 mg, 7.77 mmol), divinylbenzene (102 mg, 0.432 mmol) and THF (870 mg, 12.0 mmol) were added to a 25 mL round bottom flask equipped with a condenser. The mixture was stirred at 90 °C for 6 h. After cooling to r.t., ABN (2.80 mg, 0.017 mmol) was added. The mixture was further stirred at 90 °C for 6 h. The catalyst was crushed into a gray powder. The catalyst was collected by filtration, washed with THF (10 mL), filtered, and dried at r.t. in the air. The palladium catalyst 1 was obtained as a gray powder; yield: 640 mg (1.43 wt% of Pd).

Hydrogenation of trans-Stilbene

trans-Stilbene (180 mg, 1.00 mmol) and 1 (37.0 mg, 0.5 mol% Pd) were mixed in THF (5 mL). The mixture was stirred for 1 h at r.t. under a H$_2$ balloon. Hexane was added to the mixture, and the catalyst was filtered and washed with Et$_2$O. Removal of volatiles from the filtrate gave analytically pure 1,2-diphenylethane; yield: 182 mg (~100%).

Coupling of Iodobenzene with Phenylboronic Acid

Iodobenzene (204 mg, 1.00 mmol), Na$_2$CO$_3$ (530 mg, 5 mmol), phenylboronic acid (183 mg, 1.50 mmol), Pd(PPh$_3$)$_4$ (99.4 mg, 0.086 mmol), butan-1-ol (64.0 mg, 0.864 mmol), styrene (156 mg, 1.50 mmol), and DMF (5 mL) were added to a 25 mL flask equipped with a grease-free high-vacuum stopcock. The flask was filled with argon. The mixture was stirred at 50 °C for 12 h, the mixture was further stirred at 110 °C for 20 h, the mixture was filtered through a glass filter. H$_2$O (4 mL), and DMF (4 mL) were added to a 50 mL round bottom flask equipped with a condenser. The mixture was stirred for 1 h at r.t. in the air. The palladium catalyst 1 was obtained as a gray powder; yield: 640 mg (1.43 wt% of Pd).

Aerobic Oxidation of Benzyl Alcohol

To a solution of benzyl alcohol (108 mg, 1.00 mmol) in toluene (5 mL), was added 1 (37.0 mg, 0.5 mmol Pd), and the mixture was heated at 80 °C for 9 h under air. The catalyst was filtered and washed with acetone.

Acknowledgment

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References

(2) (a) Lysén, M.; Köhler, K. *Synthesis* 2006, 692.
   (b) Shokouhiimehr, M.; Kim, J.-H.; Lee, Y.-S. *Synlett* 2006, 618.
   (c) He, H.-S.; Yan, J.-J.; Shen, R.; Zhuo, S.; Toy, P. H. *Synlett* 2006, 563.
   (d) Uozumi, Y.; Kikuchi, M. *Synlett* 2005, 1775.
(7) Pd nanoparticles were generated from Pd(PPh₃)₄ in a mixture of butan-1-ol and THF before the polymerization with AIBN.


(9) Ph₃PO was recovered from the filtrate in more than 90% yield.

(10) In the cases of butan-2-ol and tetra(ethylene glycol), the resulting catalysts showed 26% of the activity of 1 and 44%, respectively.

(11) In the combinations of methacrylic acid and ethylene glycol dimethacrylate, methyl acrylate and ethylene glycol dimethacrylate, and acrylamide and 2,3-dimethylbuta-1,3-diene, the resulting catalysts showed 22% of the activity of 1, 34%, 3%, respectively.

(12) In the filtrate, neither Ph₃P nor Ph₃PO were detected by ¹H NMR spectroscopy, and Pd was not detected by ICP analysis.

(13) The filtrate was clear and colorless. Thus, the Pd content in the catalyst was estimated by assuming that all the Pd in the Pd(PPh₃)₄ was entrapped in the catalyst.