

# One-pot synthesis of recyclable palladium catalysts for hydrogenations and carbon–carbon coupling reactions

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**Abstract**—Palladium nanoparticles were generated from tetrakis(triphenylphosphine)palladium in a mixture of tetra(ethylene glycol) and tetramethoxysilane (or titanium(IV) isopropoxide), then encapsulated in silica matrix (or titania matrix) by the treatment with water. The resulting heterogeneous material showed high catalytic activity in the hydrogenations of various alkene and alkynes and in the carbon–carbon cross-coupling reactions such as the Suzuki–Miyaura, the Sonogashira, the Heck–Mizoroki, and the Stille reactions.

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Palladium catalysts are used in various organic transformations.<sup>1</sup> While homogeneous palladium catalysts are often used, the difficulty in separating and reusing the catalysts hinders industrial applications. Many heterogeneous palladium catalysts have been devised for recycling mainly by immobilizing palladium moieties onto inorganic supports or organic polymers.<sup>2</sup> Palladium nanoparticles,<sup>3</sup> colloidal palladium species,<sup>4</sup> and polymer-incarcerated palladiums<sup>5</sup> have also been reported as recyclable catalysts. However, they often suffer from the problems such as low reactivity, degradation, the leaching of metal species, and difficult synthetic procedures.

Herein, we describe a simple method for preparing highly active, recyclable, and external ligand-free palladium catalysts from readily available reagents through a modified sol–gel process.<sup>6</sup> In comparison to common sol–gel entrapment methods,<sup>7</sup> the key feature of ours is the use of tetra(ethylene glycol) to stabilize Pd(0) nanoparticles produced from tetrakis(triphenylphosphine)palladium in refluxing tetramethoxysilane (or titanium(IV) isopropoxide) before the gelation with water.<sup>8,9</sup>

The resulting catalysts were highly active in the hydrogenation of various alkenes and alkynes. The catalysts

were recyclable after simple filtration. In particular, the titania-supported catalyst kept its activity even in the 15th reuse. Furthermore, they showed versatile catalytic activities in the carbon–carbon cross-coupling reactions such as the Suzuki–Miyaura, the Sonogashira, the Heck–Mizoroki, and the Stille reactions (Scheme 1).

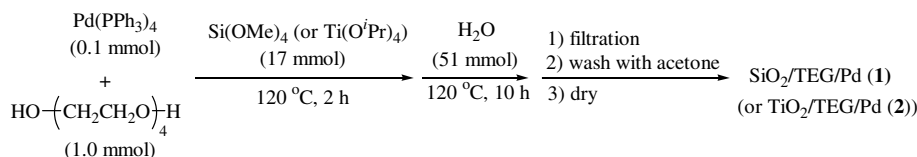
The silica gel entrapping palladium nanoparticles was prepared through a two-step procedure: (1) heating a mixture of Pd(PPh<sub>3</sub>)<sub>4</sub>, tetra(ethylene glycol), and Si(OMe)<sub>4</sub>; (2) treating the resulting black suspension with water. Washing and drying the resulting gel gave gray powder that was used as the catalyst in the following reactions. After several attempts,<sup>10</sup> we found that a 1:10:170 molar ratio for Pd(PPh<sub>3</sub>)<sub>4</sub>, tetra(ethylene glycol), and Si(OMe)<sub>4</sub>, respectively,<sup>11</sup> is adequate for producing the stable catalyst **1** reproducibly. The amount of water was set up to replace all the methoxy moieties of Si(OMe)<sub>4</sub>. Then, this procedure was applied to the preparation of a titania-supported catalyst (**2**) by using Ti(O<sup>i</sup>Pr)<sub>4</sub> instead of Si(OMe)<sub>4</sub>.

The morphologies of **1** and **2** were analyzed by transmission electron microscopy (TEM) (Fig. 1). The palladium nanoparticles are clearly shown as dark spots in gray silica (or titania) frameworks. Notably, their size is fairly regular, ranging from 2 to 5 nm.

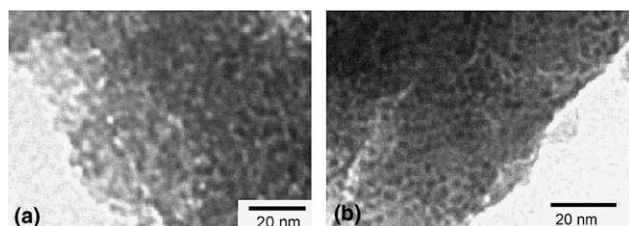
The catalysts **1** and **2** were tested on the hydrogenation of *trans*-stilbene under various conditions (Table 1). The activity of **1** was affected by solvent; it was much better

**Keywords:** Pd; Nanomaterial; Sol–gel process; Catalysts; Hydrogenation; C–C coupling reactions.

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**Scheme 1.** Preparation of recyclable palladium catalysts.



**Figure 1.** Representative TEM images of **1** and **2**: (a) SiO<sub>2</sub>/TEG/Pd (**1**); (b) TiO<sub>2</sub>/TEG/Pd (**2**).

**Table 1.** Catalytic hydrogenation of *trans*-stilbene<sup>a</sup>

Entry	Catalyst (mol%)	Solvent	Time (h)	Yield (%) <sup>b</sup>
1	<b>1</b> (2.0)	Toluene	3	100
2	<b>1</b> (2.0)	EtOAc	20	81 <sup>c</sup>
3	<b>1</b> (2.0)	THF	1.5	100 (49) <sup>d</sup>
4	<b>1</b> (0.02)	THF	120	100
5	<b>2</b> (2.0)	Acetone	2	100
6	<b>2</b> (2.0)	Toluene	3	100
7	<b>2</b> (2.0)	THF	0.5	5
8	<b>2</b> (2.0)	THF	3	100
9	<b>2</b> (2.0)	EtOAc	1	98 (68) <sup>d</sup>
10	<b>2</b> (0.02)	EtOAc	24	100

<sup>a</sup> The hydrogenation was performed on 1.00 mmol of *trans*-stilbene dissolved in 5 mL of solvent at 25 °C under 1 atm H<sub>2</sub>.

<sup>b</sup> By GC.

<sup>c</sup> After 20 h the hydrogenation didn't proceed further.

<sup>d</sup> After 30 min.

in THF than in ethyl acetate (EtOAc). However, the activity of **2** was good in all the solvents tested. Interestingly, the hydrogenation of **2** clearly showed that an activation period was needed under hydrogen. It was much slower than that with **1** at the initial stage of the first use. But the activity of **2** was increased during the first hydrogenation, and was higher than that of **1** in the second use. Notably, the higher activity of **2** (TOF = 208/h) than that of **1** (TOF = 42/h) was clearly seen when the catalyst amount was reduced to 0.02 mol%.

The catalysts could be recovered by simple filtration after the hydrogenation. It is notable that the catalysts recovered was stable in the air and reusable many times (Table 2).<sup>12</sup> Particularly, **2** retained its original activity even in the 15th use.<sup>13</sup>

The hydrogenations of various alkenes and alkynes were carried out to see the scope of **2** (Table 3). In general, the use of 2 mol% of **2** completed the hydrogenation of alkynes, 1,3-dienes, alkenes,  $\alpha,\beta$ -unsaturated carbonyl compounds in 1 h at room temperature under 1 atm H<sub>2</sub>.

**Table 2.** Recycling of **1** and **2** for the hydrogenation of *trans*-stilbene<sup>a</sup>

Cycle	1	2–5	6	7	8	9–15
% Conv <sup>b</sup> by <b>1</b>	100	100	99	96	83	—
% Conv <sup>b</sup> by <b>2</b>	98	100	100	100	100	100

<sup>a</sup> The hydrogenations were performed on 1.00 mmol of *trans*-stilbene dissolved in 5 mL of solvent (**1**: THF for 90 min; **2**: EtOAc for 60 min) at 25 °C under 1 atm H<sub>2</sub>.

<sup>b</sup> By GC.

**Table 3.** Catalytic hydrogenation of various alkynes and alkenes<sup>a</sup>

Entry	Substrate	Products	Time (h)	Yield (%) <sup>b</sup>
1	MeO <sub>2</sub> C—C≡C—CO <sub>2</sub> Me	MeO <sub>2</sub> C—CH <sub>2</sub> —CH <sub>2</sub> —CO <sub>2</sub> Me	1	100
2	Ph—C≡C—Ph	Ph—CH <sub>2</sub> —CH <sub>2</sub> —Ph	1	100
3	Ph—CH=CH—CH=CH—Ph	Ph—CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —Ph	1	100
4	Ph—CH=CH—C(=O)Me	Ph—CH <sub>2</sub> —CH <sub>2</sub> —C(=O)Me	1	99 <sup>c</sup>
5	Ph—CH=CH—C(=O)OMe	Ph—CH <sub>2</sub> —CH <sub>2</sub> —C(=O)OMe	1	100
6	Ph—CH=CH—C(=O)OH	Ph—CH <sub>2</sub> —CH <sub>2</sub> —C(=O)OH	1	100
7			12	100
8			12	100
9	Oleic acid	Octadecanoic acid	12	100
10	Cholesterol	Cholestane	24	16 <sup>d</sup>

<sup>a</sup> The hydrogenation was performed on 1.00 mmol of a substrate dissolved in 5 mL of EtOAc with 2 mol% of **2** at 25 °C under 1 atm H<sub>2</sub>.

<sup>b</sup> Isolated yield.

<sup>c</sup> As a minor product, 3-phenyl-2-butanol was produced in 1% yield.

<sup>d</sup> Determined by <sup>1</sup>H NMR.

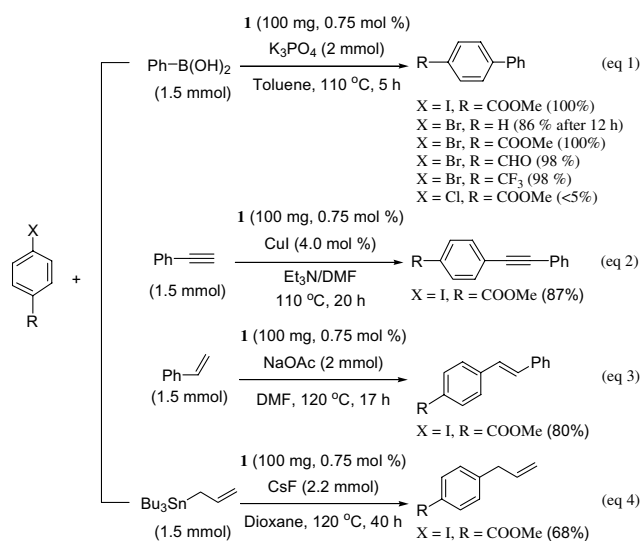
However, the hydrogenations of trisubstituted cyclic alkenes required about 12 times longer reaction time than those of simple alkynes and alkenes (entries 7 and 8). The hydrogenation of the internal carbon–carbon double bond of oleic acid was also slow, probably due to its steric hindrance (entry 9). The hydrogenation of cholesterol was distinctly slow; the conversion was only 16% even after 24 h (entry 10).

The catalytic activity of **2** was compared with those of commercially available Pd/C (5 wt%) and Pd/Al<sub>2</sub>O<sub>3</sub> (5 wt%) in the hydrogenation of neat cyclohexene at 40 °C under 1 atm H<sub>2</sub> with using 4 × 10<sup>−3</sup> mol% catalyst. After 24 h cyclohexane was produced in 30% in the reac-

tion with **2**, while in 11% in that with Pd/C and in 7% in that with Pd/Al<sub>2</sub>O<sub>3</sub>.

Then, the catalysts were applied to carbon–carbon cross-coupling reactions (Eqs. 1–4). In the Suzuki–Miyaura reaction between phenylboronic acid and bromobenzene, the activity of **1** was about two times higher than that of **2**. It is also higher than those of palladium nanospheres<sup>3b</sup> and palladium clusters.<sup>3k</sup> Thus, the other coupling reactions were carried out with **1**. While **1** was effective for the activation of aryl iodides and aryl bromides, it was not active enough toward aryl chloride. Except the Stille reaction, the yields of the coupling reactions were over 80%. The reusability of **1** was tested in the Suzuki–Miyaura reaction between phenyl boronic acid and methyl 4-bromobenzoate; the catalyst could be reused three times without losing activity.

In summary, we developed a simple method for preparing recyclable palladium catalysts from readily available reagents, and demonstrated their catalytic activities in the hydrogenation of various alkynes and alkenes and in the carbon–carbon cross-coupling reactions. Other metal-catalyzed reactions including asymmetric ones are under study.



### Acknowledgements

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- During the preparation of **1** and **2** triphenylphosphine was oxidized into triphenylphosphine oxide, which was recovered from the filtrate in more than 90% yields. Meanwhile, most of the tetra(ethylene glycol) was incorporated in the catalysts, and less than 10% of the employed amount was detected by <sup>1</sup>H NMR in the filtrate.
- The inductively coupled plasma (ICP) analysis revealed that the palladium contents of **1** and **2** are 0.59 and 0.79 wt %, respectively, and that palladium is entrapped in the catalysts in more than 95% yields.
- Following the procedures similar to that for **1**, various oligo(ethylene glycol)s were employed to make the corresponding gels to compare the catalytic activity: no ethylene glycol (30% of the activity of **1** in the hydrogenation of *trans*-stilbene), ethylene glycol (3%), di(ethylene glycol) (57%), tri(ethylene glycol) (12%), tetra(ethylene glycol) (100%), penta(ethylene glycol) (12%), hexa(ethylene glycol) (36%), poly(ethylene glycol) (M<sub>n</sub> 400: 18%; M<sub>n</sub> 550: 29%).
- When the amount of Pd(PPh<sub>3</sub>)<sub>4</sub> was reduced to 50% with maintaining the amounts of other components, the activity of the resulting catalyst decreased to about 50% of **1**. Meanwhile, increasing the amount of Pd(PPh<sub>3</sub>)<sub>4</sub> did not increase the activity.
- The palladium on charcoal would cause ignition when it is exposed to air after the use under hydrogen.
- In the filtrate palladium was not detected by ICP analysis.