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Development of a new palladium catalyst supported on phenolic resin

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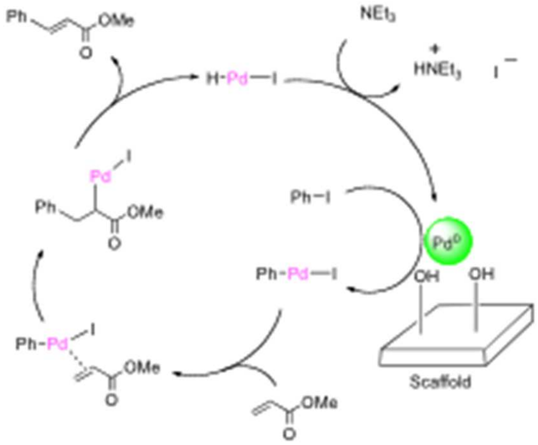
Abstract: A phenolic resin-supported palladium catalyst, in which hydroxy groups contribute to the stabilization of palladium nanoparticles, was developed. The catalyst could be used repeatedly, and thus has a large turn over number (TON). When a composite of polyethylene terephthalate and phenolic resin was employed as a support, the catalyst was easily deformed on demand.

Solid-supported catalysts have played an important role in industrial chemistry because they can be easily separated and recovered from the reaction mixture.[1] Solid-supported catalysts do not always work heterogeneously particularly for reactions using aryl iodides as substrates (Scheme 1).[2] This reaction is initiated by the oxidative addition of iodobenzene to Pd(0), which is in the form of Pd(0) nanoparticles on a scaffold. The stabilized adduct dissolves in a solution, and serves as the actual active species for the homogeneous catalysis of the reaction. After C−C bond formation, followed by reductive elimination, the Pd(0) is redeposited on the scaffold as nanoparticles. This catalytic cycle is repeated until the iodobenzene is completely consumed.[2] In this case, the solid-supported catalyst does not serve as a heterogeneous catalyst, but instead, gradually releases the homogeneous catalyst. Hence, the solid-support must adsorb and stabilize Pd(0) nanoparticles, but should also release them gradually. In addition, the support should capture free Pd(0) particles that are suspended in the reaction mixture.

The catalytic activity of solid-support catalyst is considerably influenced by the properties of the solid support. Indeed, various types of solid-supports have been employed, which add value to the original catalyst. Huang *et al.* reported that silica gel functionalized with bayberry tannin was an excellent support for maintaining catalytic activity over long time periods because the tannin stabilized the Pd nanoparticles.[3] As well as this, Funaoka's group demonstrated that the addition of lignophenols increased the discharge capacity of a batteries because they prevent the suppression of Pb particle growth.[4] The common feature of these two studies is that the addition of naturally occurring polyphenols is effective for the stabilization of metal nanoparticles.[5] However, uniform performance is difficult to obtain because naturally occurring products consist of many complex molecules that vary with location and season. These circumstances prompted us to study the development of Pd catalyst supported on phenolic resin (PR), which is thermally and chemically stable and is manufactured with uniform quality and low cost.[6] These are suitable properties for a support in organic reactions compared with other swelling polymer supports.



Scheme 1. A catalytic cycle of a solid-supported catalyst

Figure 1. Left: PR and **Pd-PR**, right: **Pd-PR-PET**

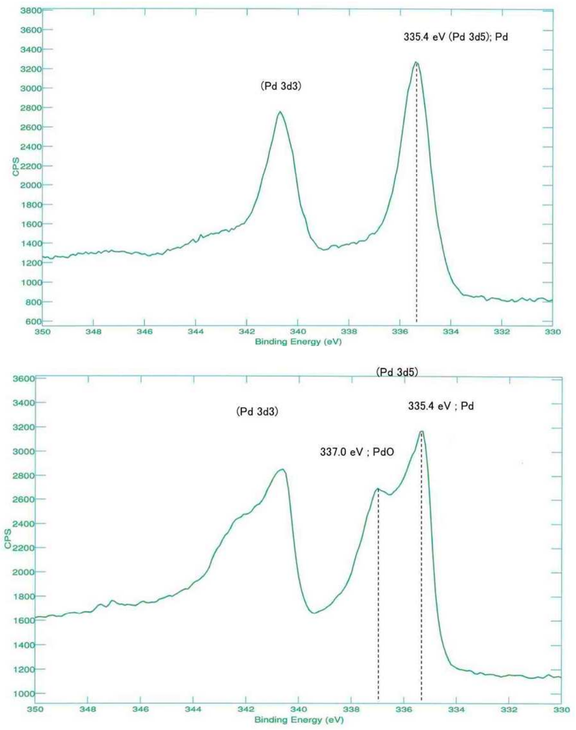


Figure 2. XPS Pd3d narrow scaned spectra of **Pd-PR** (upper) and commercially available **Pd-C** (lower)

When the spherical, cured PR† was heated in an acetonitrile solution of palladium acetate at 120 °C for 12 h in a sealed tube, the color of the PR changed to black (**Pd-PR**) (Figure 1, left). While X-ray photoelectron spectroscopy (XPS) analysis of commercially available Pd-Carbon (**Pd-C**) showed the presence of both Pd(0) and Pd(II) on the surface, only Pd(0) species was observed for **Pd-PR** (Figure 2). Although aggregation of the Pd species was observed by the scanning electron microscopy (SEM), Pd nanoparticles were also observed on the surface of the PR (Figure 3). The transmission electron microscopy (TEM) revealed a homogeneous dispersion of Pd nanoparticles of 10 nm in diameter up to a depth of 1 μm from the surface (Figure 4). These observations confirmed that immobilization of the Pd(0) nanoparticles on the PR was successively achieved.

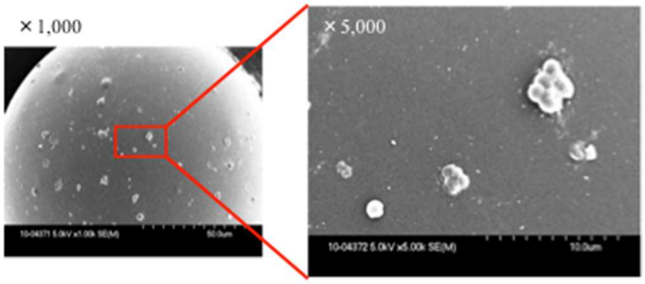


Figure 3. SEM images of **Pd-PR**

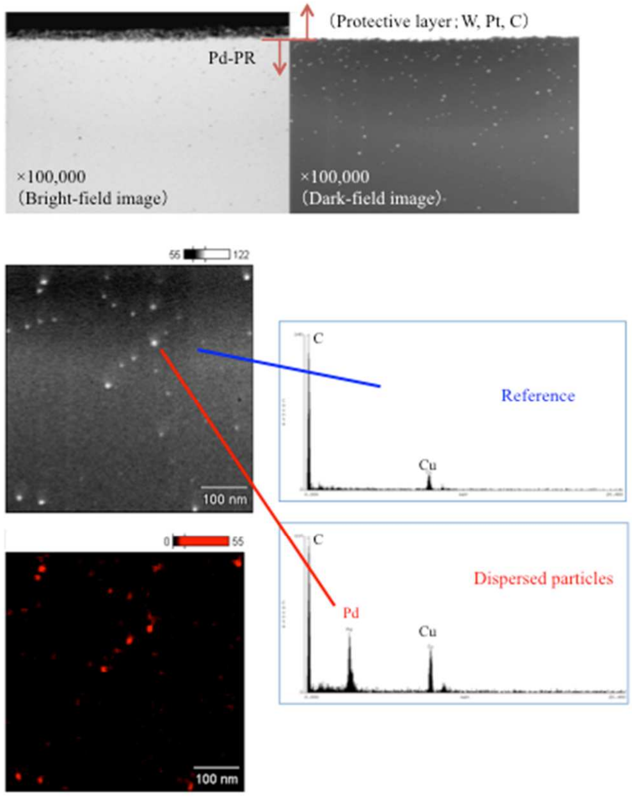
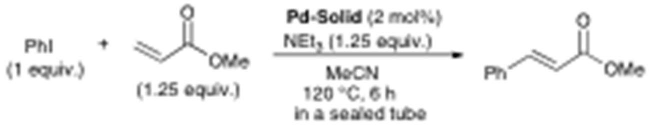


Figure 4. TEM images (upper) and EDX analysis (lower) of **Pd-PR**

Table 1. The Heck reaction using commercially available **Pd-Solid** catalysts

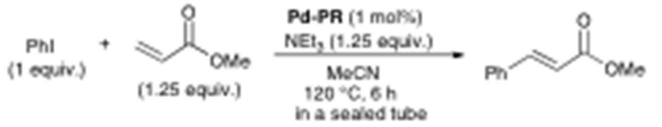


Pd-Solid	Run and Yield/%[a]					
	1	2	3	4	5	6
Pd-C	96	54	33			
Pd-Al$_2$O$_3$	99	96	85	95	47	27
Pd-BaSO$_4$	94	79	76			
Pd-HT	67	13				
Pd-EnCat	100	81	82	64	33	
Pd-Fib	89	89	80	93	81	78

[a] Determined by ^{1}H NMR. Yields over 90% are indicated with red, and those over 80% are indicated with green.

Evaluation of the catalytic activity of the solid-supported Pd catalysts should be conducted with regard to both efficiency and lifetime. For this purpose, the Heck reaction of iodobenzene and methyl acrylate was examined. Six commercially available catalysts† supported on carbon (**Pd-C**), alumina (**Pd-Al$_2$O$_3$**), barium sulfate (**Pd-BaSO$_4$**), hydrotalcite (**Pd-HT**), polyurea (**Pd-EnCat**©), and fibroin (**Pd-Fib**) were subjected to this evaluation process as controls (Table 1). Reactions using **Pd-Al$_2$O$_3$** exhibited the highest activity affording the coupling product in over 90% yield three times. In contrast, **Pd-PR** facilitated the Heck reaction more than ten times maintaining high catalytic activity even with half the amount of catalyst. From these results, PR was confirmed to be an excellent support for the immobilization of Pd nanoparticles (Table 2).

Table 2. The Heck reaction using **Pd-PR** catalyst



run	1	2	3	4	5	6	7	8	9	10
Yield/%[a]	87	93	94	94	98	99	99	99	100	95
run	11	12								
Yield/%[a]	99	87								

[a] Determined by ^{1}H NMR. Yields over 90% are indicated with red, and those over 80% are indicated with green.

The recovery of the powdery solid-supported catalyst requires filtration of the reaction mixture, which is somewhat troublesome. In order to facilitate the recovery, a bulky solid support should be used. For this reason, a polyethylene terephthalate (PET) sheet was soaked in a solution of PR and was then hardened by heating to afford PR-PET. Pd was immobilized on PR-PET in a similar way to preparation of **Pd-PR** affording **Pd-PR-PET** (Figure 1, right), with immobilization of 22% of the Pd species a confirmed by inductively coupled plasma mass spectroscopy (ICP-MS). When 1 mol% of the Pd catalyst was used, methyl cinnamate was afforded in over 80% yield 25 times with a turn over number (TON) of 26000 (96% average yield) (Table 3). The ICP-MS of the repeatedly used catalyst for 25 times indicated that 44% leaching of Pd occurred, as shown in Scheme 1. **Pd-PR-PET** facilitated the Heck reaction 9 times with a TON of 93000 (95% average yield), even with less than 0.1 mol% loading (Table 3).

Table 3. Study on the catalyst loading of **Pd-PR-PET**[a]

Catalyst loading/mol%	Repeated use[b]	Average yield/%	TON
1	25	96	26000
0.5	11	94	23000
0.1	9	95	93000
0.05	4	88	77000

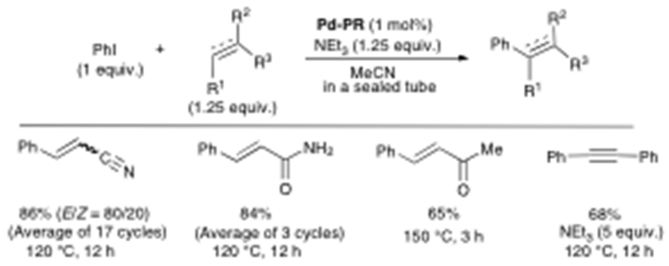
[a] The catalytic activity was evaluated by the Heck reaction of iodobenzene with methyl acrylate (1.25 equiv.) in the presence of NEt$_3$ (1.25 equiv.) in MeCN with heating at 120 °C for 12 h in a sealed tube. [b] The number of reactions affording methyl cinnamate over 80%.

Table 4. Study on the effect of phenolic hydroxy groups.

	Run and Yield/%[a]							
	1	2	3	4	5	6	7	8
Pd-RR	93	85	85	82	80	83	80	82
Pd-PR	88	81	81	77	66	64	63	65
Pd-C	83	53	53	54	53	50	56	56

[a] Determined by ^{1}H NMR. Yields over 90% are indicated with red, and those over 80% are indicated with green.

In the **Pd-PR** catalyst, phenolic hydroxy groups were thought to stabilize the Pd nanoparticles. On this basis, the resorcinol resin-supported Pd catalyst (**Pd-RR**) was employed (Table 4). While the reference catalyst, **Pd-C**, facilitated the Heck reaction only once, **Pd-PR** and **Pd-RR** afforded the coupling product in over 80% yield, under the same conditions, 4 times and 8 times, respectively. This strongly supported our hypothesis.



Scheme 2. Coupling reaction using other substrates catalyzed by **Pd-PR**

Pd-PR also catalyzed the Heck reaction for other substrates (Scheme 2). In the case of acrylonitrile, the catalyst could be used 17 times with an average yield of 86%. The catalyst facilitated the coupling reaction with acrylamide and methyl vinyl ketone to afford the corresponding phenyl-substituted alkene, respectively, though the reaction conditions are yet to be optimized. It was also confirmed that **Pd-PR** catalyzed the Sonogashira reaction producing diphenylacetylene.

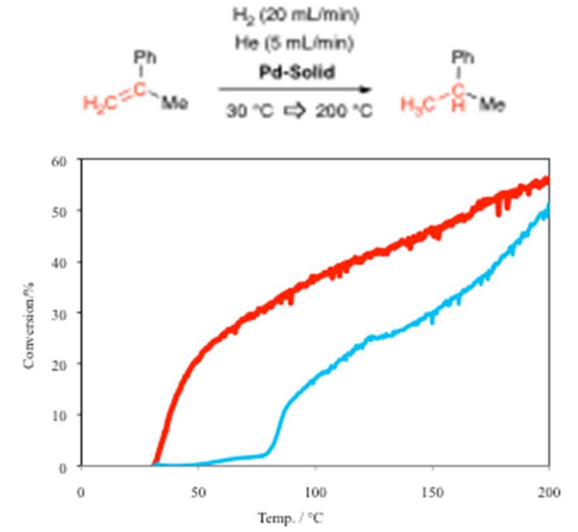


Figure 5. Hydrogenation of α-methylstyrene with elevating the temperature using **Pd-PR** (red) and **Pd-C** (blue)

The **Pd-PR** catalyst was found to be suitable for the hydrogenation of the C-C double bond of α-methylstyrene (Figure 5). The reference catalyst, **Pd-C**, did not enable the reaction to occur below 80 °C, and the conversion reached 50% only upon heating to 200 °C. In contrast, the hydrogenation occurred at 30 °C, and the conversion was 50% at 167 °C. Hence, the **Pd-PR** is has been shown to be superior to the commercially available **Pd-C** catalyst.

As demonstrated, the **Pd-PR** was suitable for repeated use in the Heck reaction with conservation of high catalytic activity. The catalyst is: 1) stable to oxygen and water, and can thus be treated in air without special care; 2) available with uniform quality at low cost and; 3) easily prepared, and can be recovered from the reaction mixture and reused repeatedly without any special treatment. In addition, the support can be deformed easily on demand. The above-mentioned properties of **Pd-PR** are advantageous for its practical use; hence, the **Pd-PR** catalyst is an alternative candidate to the commonly used solid-supported catalysts.

Experimental

General

The ^{1}H NMR spectra were measured on a Bruker Ascend-400 at 400 MHz with TMS as an internal standard. Scanning Electron Microscope (SEM) observation was performed using Hitachi SEM S-4700. Transmission electron microscope (TEM) observation was performed using Hitachi TEM HF-2200. The X-ray photoelectron spectroscopy (XPS) was measured by ThermoFisher Escalab-220iXL. Inductively coupled plasma mass spectroscopy (ICP-MS) was recorded on Shimadzu ICPS-8100. The evaluation of the catalytic activity for hydrogenation was performed using FRONTIER-LAB Single μ-Reactor Rx-3050SR. All the reagents and solvents were commercially available and were used as received. Sumiliteresin PR-ACS-100 and PR-50087 (Sumitomo Bakelite Co., Ltd.) were used for **Pd-PR** and **Pd-PR-PET**, respectively. Six kinds of **Pd-Solid** catalysts were purchased from Wako Pure Chemical Industries, Ltd. All products are also commercially available, and the structure was confirmed by comparison of their spectral data with those of authentic samples.

Preparation of the Pd-PR catalyst

In a screw-capped test tube, phenolic resin (PR, 500 mg) was put in a solution of palladium acetate (1 mg, 4 mmol) in acetonitrile (3 mL). After sealing, the resultant mixture was heated at 120 °C for 12 h on an oil bath. The blackly changed resin was collected by filtration, and washed with acetonitrile (3 mL × 3) to afford **Pd-PR**.

Preparation of the Pd-PR-PET catalyst

To a solution of phenolic resin in acetone (50% *v*/*v*), a sheet of polyethylene terephthalate (PET, 1cm × 1 cm) was soaked for 1 min. The sheet was dried in the air at room temperature for 2 days, and further dried at 90 °C for 30 min. in a dry oven. Furthermore, the sheet was heated at 150 °C for 90 min. for hardening of the phenolic resin.

In a screw-capped test tube, a PET sheet covered with phenolic resin (PR-PET) was put in a solution of palladium acetate (1 mg, 4 mmol) in acetonitrile (3 mL). After sealing, the resultant mixture was heated at 120 °C for 12 h on an oil bath. The blackly changed sheet was picked up with a tweezers, and washed with acetonitrile (3 mL × 3) to afford **Pd-PR-PET**.

ICP analysis

A **Pd-PR-PET** was soaked in 15 *M* nitric acid at room temperature for 1 day. The nitric acid solution was moved to a volumetric flask, and the total volume was adjusted to 100 mL by adding water. The solution was subjected to the measurement of ICP-MS.

Heck Reaction

In a screw-capped test tube, to a solution of iodobenzene (23 μL, 0.2 mmol), methyl acrylate (23 μL, 0.25 mmol) and triethylamine (35 μL, 0.25 mmol) in acetonitrile (3 mL), catalyst **Pd-Solid** containing 1 or 2 mol% of Pd was added. After sealing, the resultant mixture was heated at 120 °C for 6 h using an oil bath. In the case of **Pd-PR-PET**, the catalyst was recovered with tweezers from the reaction mixture. When the catalyst was powder, the recovery was performed by filtration. After evaporation, the residue was dissolved in deuterated chloroform, and the yield of methyl cinnamate was estimated by ^{1}H NMR, in which the integral value was compared with that of an internal standard, 1,1,2,2-tetrachloroethane. The recovered **Pd-Solid** catalyst was used for the next reaction without any special treatment.

When other substrate was used, the experiment was conducted in a same way.

Hydrogenation of α-methylstyrene

The evaluation of catalytic activity for the hydrogenation was performed using the equipment as shown in Figure 6. α-Methylstyrene vaporized at room temperature under atmospheric pressure was passed trough a column purged with catalyst (5 wt% of Pd, 1 mg) using a mixed gas of hydrogen (20 mL/min) and helium (5 mL/min). Then, the column was heated with elevating the temperature 10 °C/min rate, and exhaust gas was analyzed using GC-MS every 2 sec. The catalytic activity was evaluated by comparing the conversion of α-methylstyrene to isopropylbenzene.

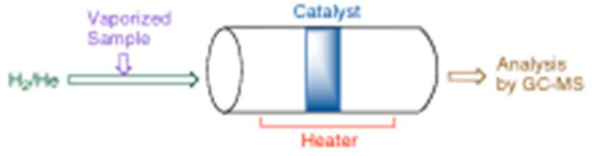


Figure 6. Rapid catalyst screening reactors

Notes and references

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[b] Research Center for Material Science and Engineering, Kochi University of Technology, Tosayamada, Kami, Kochi 782-8502, Japan.
[c] Sumitomo Bakelite Co., Ltd., Takayanagi, Fujieda, Shizuoka, 426-0041, Japan.

† Sumiliteresin PR-ACS-100 and PR-50087 (Sumitomo Bakelite Co., Ltd.) were used for **Pd-PR** and **Pd-PR-PET**, respectively. Six kinds of **Pd-Solid** catalysts were purchased from Wako Pure Chemical Industries, Ltd.

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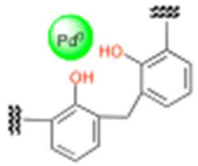
Graphical Abstract



Palladium catalyst supported on phenolic resin

- Stable to oxygen and water
- Repeatedly usable
- Easily prepared and recovered from the reaction mixture
- Deformed on demand