Supplementary Information

Controlled Synthesis of Hydroxyapatite-Supported Palladium Complexes as Highly Efficient Heterogeneous Catalysts

Kohsuke Mori, Kazuya Yamaguchi, Takayoshi Hara, Tomoo Mizugaki, Kohki Ebitani
and Kiyotomi Kaneda*

*Department of Chemical Science and Engineering,
Graduate School of Engineering Science, Osaka University,
1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan.
Phone and Fax: +81-6-6850-6260, E-mail: kaneda@cheng.es.osaka-u.ac.jp*

The synthesis of hydroxyapatite-supported Pd catalysts: $(\text{NH}_4)_2\text{HPO}_4$ (40.0 mmol) was dissolved in deionized water (150 mL) and pH was adjusted to 11 with aqueous NH_3 solution. To a solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (66.7 mmol) in deionized water (120 mL) adjusted to pH 11 with aqueous NH_3 solution was added drop-wise over 30 min into the above solution with vigorous stirring at room temperature, and then the obtained milky solution was heated at 90 °C for 10 min. The precipitate was filtered, washed with deionized water, and dried at 110 °C, giving $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ($Z = 0$, HAP-0). $\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH})$ ($Z = 1$, HAP-1) was also prepared by changing the Ca/P-ratio from 1.67 to 1.50 in the above starting solutions. 2.0 g of the HAP-0 was stirred at 25 °C for 3 h in 150 mL of acetone solution of $\text{PdCl}_2(\text{PhCN})_2$ (2.67×10^{-4} M). The obtained slurry was filtered, washed with acetone and dried under vacuum, yielding 2.01 g of the PdHAP-0 (Pd content: $0.02 \text{ mmol} \cdot \text{g}^{-1}$). The PdHAP-1 (Pd content: $0.015 \text{ mmol} \cdot \text{g}^{-1}$) was also prepared by the same method using the HAP-1 in place of the HAP-0.

A typical example for the oxidation of alcohols: Into a reaction vessel with a reflux condenser were placed PdHAP-0 (0.1 g, Pd: 2 μmol), 1-phenylethanol (0.12 g, 1 mmol) and trifluorotoluene (5 mL). The resulting mixture was stirred at 90 °C under 1 atm of O_2 . The progress of reaction was monitored by GC analysis. After 1 h, 98% yield of acetophenone was

obtained. For the recycling experiment, the reaction mixture was centrifuged after the fresh run, and the solution was removed from the spent PdHAP-0 by a syringe. When another 1-phenylethanol (1 mmol) and trifluorotoluene (5 mL) were continuously added, both the second and third reactions gave acetophenone in > 97 % GC yields, respectively. When the spent PdHAP-0 catalyst was washed with solvent and dried under vacuum, a moderate yield (43 %) was obtained in the second run. However, it was found that the catalytic activity was completely retained only by the addition of small amounts of KCl or NaCl. For example, addition of 5 equivalents of KCl relative to Pd gave acetophenone in > 97% GC yield in the second and third runs under the above fresh reaction conditions.

A procedure of the large-scale oxidation of 1-phenylethanol: Into a reaction vessel with a reflux condenser were placed 1-phenylethanol (30.5 g, 250 mmol) and PdHAP-0 (0.05 g, Pd: 1 μ mol). The resulting mixture was stirred at 160 °C in the presence of O₂ under Dean-Stark conditions. After 24 h, PdHAP-0 was separated by a filtration, and then the distillation of the filtrate gave pure acetophenone (28.3 g, 94% yield).

A typical example of the Heck coupling reaction: PdHAP-1 (0.05 g, Pd: 0.75 μ mol) and K₂CO₃ (6.2 g, 45 mmol) were placed into a reaction vessel with a reflux condenser. Under Ar atmosphere, *N*-methylpyrrolidone (NMP) (50 mL), bromobenzene (5.9 g, 37.5 mmol), and styrene (4.7 g, 45 mmol) were added, and then the resulting mixture was stirred at 130 °C. The progress of reaction was monitored by GC analysis. After 24 h, 94% yield of stilbene (*E* : *Z* = 15 : 1) was obtained. For recycling experiments, fresh reaction using bromobenzene (2 mmol), styrene (2.4 mmol), K₂CO₃ (2.4 mmol), NMP (5 mL), and PdHAP-1 (0.1 g, Pd: 1.5 μ mol) was carried out at 130 °C under Ar atmosphere. After 4 h, the reaction mixture was centrifuged and the liquid phase was decanted. The residual solid catalyst was again added to the substrate and reacted under identical conditions. The first, the second, and the third runs gave stilbene in > 92% GC yields.

A typical example of the Suzuki coupling reaction: PdHAP-1 (0.05 g, Pd: 0.75 μ mol), K₂CO₃

(6.2 g, 45 mmol), and phenylboronic acid (5.5 g, 45 mmol) were placed into a reaction vessel with a reflux condenser. Under Ar atmosphere, *o*-xylene (50 mL) and 4-bromoanisole (7.0 g, 37.5 mmol) were added, and the resulting mixture was stirred at 120 °C. The progress of reaction was monitored by GC analysis. After 6 h, 91 % yield of 4-methoxybiphenyl was obtained.

Characterization by Pd K-edge x-ray absorption fine structure (XAFS): X-ray absorption spectra were recorded using a fluorescence-yield collection technique at the beam line 01B1 station with attached Si (311) monochromator at SPring-8, JASRI, Harima, Japan (prop. No. 2001A0563-UX-np). Fluorescence-yield was collected at room temperature using the 19-element solid-state detector. Details of data analysis are referred to the reported procedure. see T. Tanaka, H. Yamashita, R. Tsuchitani, T. Funabiki, S. Yoshida, *J. Chem. Soc., Faraday Trans.* **1988**, *84*, 2987. Results of curve-fitting analysis for PdHAP catalysts are as shown in Table 3 and Figure 2. Inverse Fourier transforms were performed for the regions of 0.9-2.2 Å in Fig. 1A, 0.9-2.0 Å in Fig. 1B, 1.95-3.0 Å in Fig. 1C, and 0.9-2.0 Å in Fig. 1D.

Table 3. Curve-fitting analysis for PdHAP catalysts

Sample	Shell	C.N. ^a	R (Å) ^b	$\Delta\sigma$ (Å ²) ^c
PdHAP-0 (A)	Pd-Cl	2.0	2.36	0.0087
	Pd-O(1)	2.1	2.01	0.0006
	Pd-O(2)	3.0	2.37	0.0199
PdHAP-1 (B)	Pd-O(1)	4.2	2.01	0.0031
	Pd-O(2)	3.0	2.34	0.0342
Recovered PdHAP-0 (C)	Pd-Pd	7.0	2.77	0.0018
Recovered PdHAP-1 (D)	Pd-O(1)	4.1	2.01	0.0020
	Pd-O(2)	3.0	2.33	0.0233

^a Coordination number. ^b Interatomic distance. ^c Difference between Debye-Waller factor of PdHAP and that of the reference sample.

Figure 2. (a) Inverse Fourier-transforms of k^3 -weighted Pd K-edge EXAFS experimental data for (A) PdHAP-0, (B) PdHAP-1, (C) recovered PdHAP-0, and (D) recovered PdHAP-1 for the oxidation of 1-phenylethanol. The dotted line shows the results of a curve-fitting analysis.

Transmission electron micrograph (TEM) analysis: TEM images and size distribution diagram of the Pd particles for the recovered PdHAP-0 catalyst after the oxidation are shown in Figure 3. Oxidation of 1-phenylethanol (1 mmol) was conducted with PdHAP-0 (0.1 g, Pd: 2 μ mol) in trifluorotoluene (5 mL) at 90 °C for 1h under O₂ atmosphere.

Fig. 3. Transmission electron micrograph and size distribution diagram of the Pd particles for the recovered PdHAP-0 catalyst.