Sonochemical Preparation of Size-Controlled Palladium Nanoparticles on Alumina Surface

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(Received December 18, 1998; CL-980937)

A new method for the preparation of Pd nanoparticles immobilized on alumina at room temperature by ultrasonic irradiation of an aqueous solution of tetrachloropalladate(II) is reported. The size of Pd particles can be controlled by changing the type of alcohol and the amount of coexisting alumina.

Ultrasonic irradiation of a liquid provides acoustic cavitation which is comprised of the formation, growth and collapse of bubbles in a liquid. When the cavitation bubbles are collapsing, the inside of the bubbles reach high temperatures (several thousands of degrees) and high pressures (hundreds of atmospheres) together with a shock wave.[1] Using these unique and extreme conditions as a reaction site, the formation of a novel material can be expected. Recently, the application of ultrasound for the syntheses of polymeric and inorganic materials and the elimination of pollutants has been extensively studied.[2] Pd catalysts are well known to exhibit high activity for hydrogenation and oxidation, and the activity generally depends on their particle size, shape, etc.[3] These parameters affecting the activity are attributed to the preparation methods and conditions.

In this paper, we report a new method for the preparation of size-controlled Pd nanoparticles on alumina at room temperature by ultrasonic irradiation of an aqueous solution of tetrachloropalladate (II) (Pd(II)). The formation processes of the supported materials are suggested by analyzing the irradiated solution and products.

Ultrasonic irradiation was carried out using an ultrasonic generator (200 kHz, 6 W/cm^2) and a 65 mmϕ barium titanate oscillator. The details of the irradiation set-up are described in a previous paper.[4] An argon purged aqueous solution of $PdCl_2 \cdot 2NaCl \cdot 3H_2O$ (1 mM, 65 mL) containing α-alumina with an average diameter of 0.5 μm (2.02~10.5 g/L) was sonicated at 20 ℃. An alcohol, which acts as an effective accelerator of the reduction of Pd(II), was injected into the solution using a micro-syringe through the septum just before the irradiation. During the irradiation, the vessel was closed.

Figure 1 shows the change in the absorption spectra of the sample solution during ultrasonic irradiation. Each of them is filtered using a membrane filter with a pore-size of 0.2 μm to remove the alumina powders and colored by using the NaI colorimetric method.[5] The absorption peak of $[PdI_4]^{2-}$ corresponding to Pd(II) was observed at 408 nm. The peak height smoothly decreased with irradiation time, indicating that the reduction of Pd(II) readily proceeded. The color of alumina powders gradually changed from white to black due to the irradiation. These results suggest the formation of Pd particles on the surface of the alumina. The formation of metallic Pd was also confirmed by its X-ray diffraction pattern.[6]

It has been reported[5] that the sonochemical reduction of Pd(II) in the presence of an organic additive proceeds via the following equations,

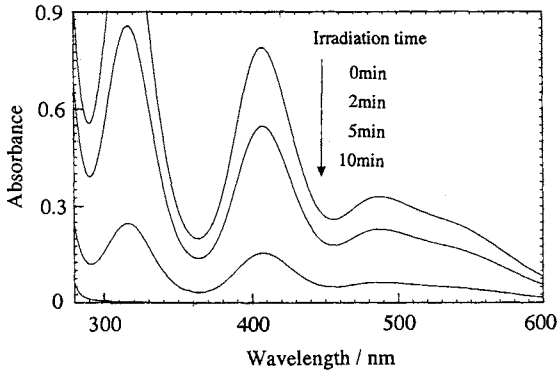

Figure 1. Absorption spectra of irradiated sample solution colored by NaI. Sample is diluted 5 times with water. Cell length: 0.5 cm. Conditions: 1 mM Pd(II), 2.02 g/L Al_2O_3, 20 mM 1-propanol.

$$H_2O \xrightarrow{)))} \cdot OH + \cdot H \quad (1)$$

$$RH + \cdot OH\ (\cdot H) \rightarrow \cdot R_{ab} + H_2O\ (H_2) \quad (2)$$

$$RH \xrightarrow{)))} \cdot R_{py} + \cdot H \text{ etc.} \quad (3)$$

$$Pd(II) + \text{Reducing radicals} \rightarrow \rightarrow Pd(0) \quad (4)$$

where RH denotes an organic additive. Eqs. (1) to (3) indicate the sonochemical formation of the reducing radicals: (1) $\cdot$H is formed from water sonolysis, (2) $\cdot R_{ab}$ is formed from the abstraction reaction of RH with $\cdot$OH or $\cdot$H, and (3) $\cdot R_{py}$ is formed via RH pyrolysis. Finally, the reduction of Pd(II) proceeds by Reducing radicals such as $\cdot$H, $\cdot R_{ab}$ and $\cdot R_{py}$.

From the result shown in Figure 1, even in a heterogeneous solution containing alumina powders, it was suggested that hot spot bubbles were sufficiently generated as in a homogeneous solution so that the reduction successfully proceeded.

The rates of reduction were different among the different alcohols. In the case of a 20mM alcohol, the rates (μM/min)

Table 1. Average size and standard deviation of Pd particles formed and rate of Pd(II) reduction by ultrasonic irradiation[a]

Condition Pd/Al_2O_3[b], Alcohol	Average size (nm)	Standard deviation	Rate[c] (μM/min)
1 wt%, 1-Propanol	6.8	1.8	120
3 wt%, 1-Propanol	7.1	2.2	130
5 wt%, 1-Propanol	8.6	2.8	130
5 wt%, Ethanol	10.0	2.9	50
5 wt%, Methanol	11.3	5.8	30

[a] Irradiation time: 30 min, Pd(II): 1 mM, alcohol: 20 mM. [b] Weight Ratio. [c] Average rate for initial 5 min irradiation.

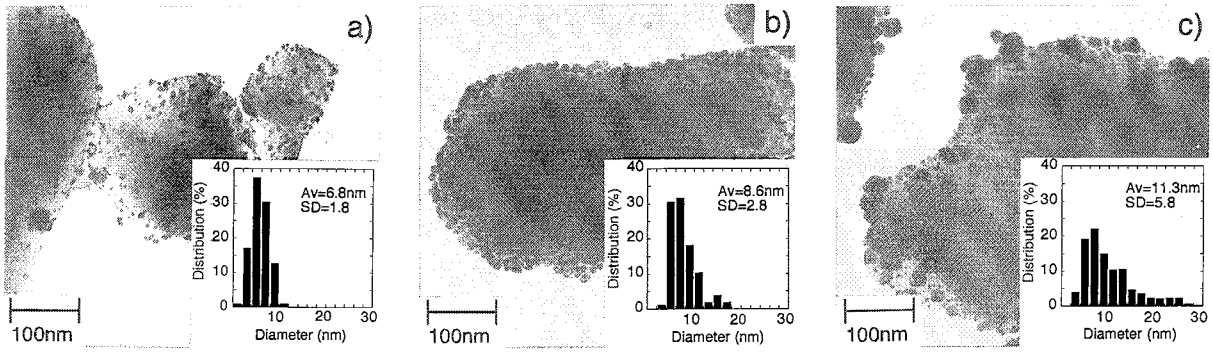

Figure 2. TEM photographs of products and size distribution of Pd particles formed by 30 min irradiation.
Conditions: 1 mM Pd(II), 20 mM alcohol. a) 1 wt% Pd/Al_2O_3, 1-propanol, b) 5 wt% Pd/Al_2O_3, 1-propanol, c) 5 wt% Pd/Al_2O_3, methanol.

were in the order of methanol: 30, ethanol: 50, 1-propanol: 130, at an initial concentration of 1mM Pd(II) and 2.02 g/L alumina powders (corresponding to 5 wt% Pd/Al_2O_3).

Figure 2 shows transmission electron micrographs of the products[7] and the size distribution of the formed Pd particles on alumina. It was confirmed that the Pd particles were of nanometer size and highly dispersed on the surface of the alumina. The average size, standard deviation of the formed Pd particles and the rate of Pd(II) reduction under several conditions are also summarized in Table 1. In this experiment, the concentrations of Pd(II), alcohol and the irradiation time are fixed at 1 mM, 20 mM and 30 min, respectively.

As shown in Figures 2b and 2c and Table 1, the size of the formed Pd particles and their distribution were dependent on the kind of alcohols. As mentioned above, alcohol is an important additive for controlling the rate of reduction. Therefore, it is suggested that smaller particle would be obtained when the rate of Pd nucleation is faster. In addition, as the hydrophobicity of the alcohol increases, it is known to behave as a stabilizer for the colloidal particles to avoid aggregation, such as a surfactant. From the result of a stability experiment of the Pd colloidal particles prepared by the conventional method, the particles were found to be slightly stabilized in the presence of 1-propanol compared with in pure water.[8] This result also implies that a more hydrophobic alcohol somewhat retards the growth of the particles in an aqueous solution.

The effect of alumina on the formation of Pd particles was investigated. These results are also shown in Figures 2a and 2b and Table 1. The size of the particles and its standard deviation became smaller with the increasing amount of alumina in the order of 5 wt%Pd (Al_2O_3: 2.02 g/L) < 3 wt%Pd (3.44 g/L) < 1 wt%Pd (10.5 g/L). Since the rate of reduction was almost the same among them, the growth and the agglomeration of the Pd particles in solution would be suppressed by its adsorption onto alumina so that the size of the formed Pd particles was smaller as the amount of alumina increased.

To discuss the formation processes of the supported materials, a preliminary adsorption experiment was carried out.[9] The result indicated that the adsorption of Pd(II) on alumina could be excluded in our irradiation system, because the rate of adsorption is very slow compared with that of Pd(II) reduction by ultrasound.[9] Therefore, the nucleation of Pd(0) occurred in the bulk solution (eq. (4)), and then the growth (eq. (5)) and the immobilization (eq. (6)) of the Pd particles would proceed as follows,

$$nPd \rightarrow \rightarrow Pd_n \quad (5)$$

$$Pd_n + Al_2O_3 \rightarrow Pd_n \text{ immobilized on } Al_2O_3 \quad (6)$$

where Pd_n denotes a Pd particle. Since the size of the particles is affected by the type of alcohol and the coexisting amount of alumina, the growth of the Pd particles also occurs in the bulk solution. In this method, it is noted that the formed Pd particles are selectively immobilized only on the surface of the alumina.

We were able to readily prepare highly dispersed Pd nanoparticles immobilized on alumina at room temperature by the sonochemical reduction of Pd(II) in an aqueous suspension. The results obtained in the present experiments suggest that the sizes of the Pd particles could be more accurately controlled by selecting the types and concentrations of the organic additive and the support.

This work was partially supported by The Sound Technology Promotion Foundation.

References and Notes

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4 Y. Nagata, Y. Mizukoshi, K. Okitsu, and Y. Maeda, *Radiat. Res.*, **146**, 333 (1996): A cylindrical glass vessel (volume: 190 mL, diameter: 55 mmϕ) was used for ultrasonic irradiation, which had a silicon rubber septum for gas bubbling or sample extraction without exposing the sample to air. The bottom of the vessel was planar and 1mm in thickness. The vessel was fixed on the oscillator. Under our experimental conditions, the rate of formation of OH radicals in the sonolysis of pure water is estimated to be ca. 20 μM/min which is measured by Fricke dosimetry.
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6 The XRD pattern was measured by Rigaku RINT-2200. No other peaks attributed to palladium oxide or other compounds of palladium were found.
7 The product was examined using a JEOL JEM-100S electron microscope at an acceleration voltage of 100 kV.
8 The stability of the Pd colloidal particles prepared by a $NaBH_4$ reduction of Pd(II) in the presence of an alcohol was investigated. The occurrence of the aggregation was monitored by a spectrophotometer.
9 The adsorption experiment of Pd(II) on alumina was carried out at 20 ℃ in an aqueous solution of 1 mM Pd(II) and 2.02 g/L alumina. The rate of the adsorption was ca. 6 μM/min for initial 30 min.