# Sonochemical Preparation and Catalytic Behavior of Highly Dispersed Palladium Nanoparticles on Alumina

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Palladium nanoparticles dispersed on $Al_2O_3$ were prepared via the sonochemical reduction of tetrachloropalladate(II) (Pd(II)) in an aqueous solution. The reduction of Pd(II) to metallic Pd successfully proceeded, even in the presence of $Al_2O_3$ powder, by ultrasonic irradiation at 200 kHz. The rates of Pd(II) reduction strongly depended on the type of alcohol additive, which acts as an effective accelerator for Pd(II) reduction. The dispersion of metallic Pd particles on the $Al_2O_3$ surface was appreciably enhanced by increasing the rate of reduction. By UV−visible, pH, and transmission electron microscopy measurements, the major pathway in the formation of Pd nanoparticles on $Al_2O_3$ was speculated to proceed via the following three steps: (1) the reduction of Pd(II) ions proceeds with reducing radicals formed by sonolysis of water and alcohol molecules, resulting in the formation of Pd nuclei, (2) the growth and/or the agglomeration of the Pd nuclei rapidly occurs to form Pd nanoparticles, and (3) the Pd particles are simultaneously adsorbed onto the $Al_2O_3$ surface. The catalytic activities of the Pd nanoparticles prepared by sonochemical reduction were investigated for the hydrogenation of olefins at room temperature. The rates of hydrogenation over these catalysts were much higher than those over a conventionally prepared Pd/$Al_2O_3$ catalyst and a commercially available Pd black.

## Introduction

During the past decade, there have already been numerous publications about physicochemical methods for the preparation of nanostructured materials, i.e., chemical reduction methods with various strong reductants,[1−3] photochemical processes[4] or radiation−chemical reduction,[5] and evaporative methods.[6] High-power ultrasound has been applied widely in the preparation of nanostructured materials because of unique phenomena induced by ultrasonic cavitation.

The cavitation, which is caused by ultrasonic irradiation of a liquid, comprises the formation, growth, and collapse of bubbles in a liquid. When the cavitation bubbles are violently collapsing, the temperature and pressure of the bubbles reach several thousands of degrees and hundreds of atmospheres, respectively, accompanied by shock wave generation.[7,8] The formation of novel materials can be expected under such extreme conditions. Recently, the application of ultrasound in the syntheses of various nanostructured materials with high surface areas and their interesting properties have been extensively studied. Suslick et al.[9] reported that amorphous metals, alloys, metal carbides, and sulfides of transition elements, which were difficult to prepare by conventional thermal methods, were successfully synthesized in the sonochemical decomposition of volatile metal carbonyls in an organic solvent. These materials exhibited high catalytic activities for the Fischer−Tropsch reaction, dehydrogenation of saturated hydrocarbons, etc. In addition, Gedanken and co-workers[10] reported the formation of various kinds of metal oxides, such as nanosize semiconductor and magnetic materials, by using a similar procedure. There are many reports involving the formation of metal particles and powders in nonaqueous solutions due to the action of ultrasound. However, only a limited number of reports concerned the preparation of these materials in aqueous solution. In addition, to our knowledge there are very few reports related to the control of the rate of formation and the size of particles formed in the nanometer range.

To fabricate a nanostructured material in water, it seems reasonable to use metal ions as a starting material rather than a metallic material because several kinds of excellent techniques are now available for colloidal dispersion systems composed of aqueous solu-

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tions of metal ions.[3,11] In the sonochemical process, it is well-known that the reduction of noble metal ions proceeds via the sonolysis of water and organic additives. Henglein and co-workers[12] first reported the reduction of $AuCl_4^-$ and $Ag^+$ in an aqueous solution by ultrasonic irradiation under various $Ar-H_2$ conditions, suggesting that the reduction was strongly enhanced at about 20 vol % $H_2$. Nagata et al.[13] revealed that the reduction of $Ag^+$ ions to metallic Ag under a pure argon atmosphere proceeded both by H atoms formed in the sonolysis of water and by secondary reducing radicals generated from the abstraction reaction of organic additives with OH radicals and H atoms. The formation of colloidal Ag nanoparticles could also be shown when the reduction was carried out in the presence of a suitable protective agent such as a surfactant. Recently, several types of metal nanoparticles have been prepared by use of various kinds of surfactants.[14−16]

We have already reported a new application of organic radicals, which were formed from the sonochemical decomposition of various organic additives such as surfactants, water-soluble polymers, and alcohols, in the reduction of noble metal ions to their metallic nanoparticles in aqueous solutions.[15−17] A more detailed mechanism for the formation of Pd nanoparticles and their immobilization on alumina is examined in the present report. In addition, it was proved that the rate of Pd formation and the size of Pd particles on $Al_2O_3$ could be controlled. The catalytic activity of the $Pd/Al_2O_3$ obtained by the sonochemical method was also investigated for the hydrogenation of olefins at ambient temperatures.

## Experimental Section

Reagent-grade $PdCl_2{\cdot}2NaCl{\cdot}3H_2O$, NaI, methanol, ethanol, 1-propanol, 1-hexene, Pd black, and $\alpha$-$Al_2O_3$ with a nominal particle size of 0.5 $\mu$m were purchased from Wako, and *trans*-3-hexene was obtained from Aldrich. These chemicals were used without further purification. Ultrasonic irradiation was carried out at 20 °C in a water bath with an ultrasonic generator (Kaijo 4021, 200 kHz, 6W/cm$^2$) and a 65 mm $\phi$ barium titanate oscillator. The irradiation setup is shown schematically in Figure 1. For ultrasonic irradiation a cylindrical glass vessel (volume 190 mL) was used, which had a port covered by a silicon rubber septum for gas bubbling or sampling without exposing the sample to air. The bottom of the vessel was planar, 1 mm in thickness, and 55 mm $\phi$ in diameter. The vessel was fixed directly on the oscillator. During operation, the rate of $H_2O_2$ formation in the sonolysis of pure water was estimated by Fricke dosimetry to be ca. 10 $\mu$M/min in the Ar atmosphere.[16a]

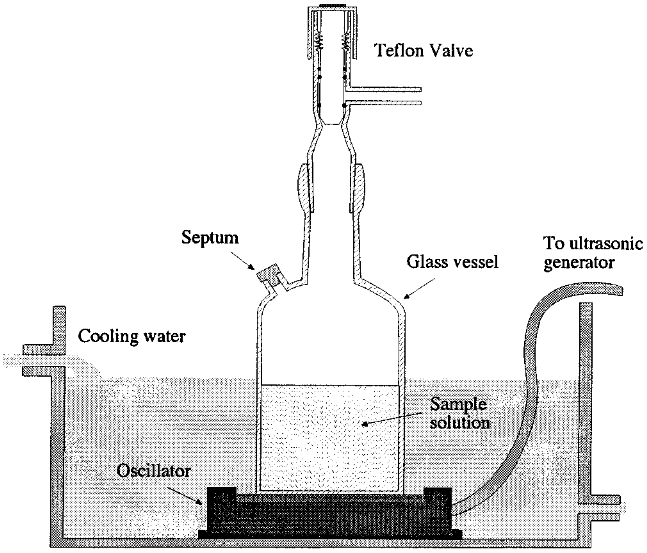

**Figure 1.** Schematic of ultrasonic irradiation setup in the present work.

An aqueous solution of Pd(II) (1 mM, 65 mL) containing $\alpha$-$Al_2O_3$ (2.02 or 10.5 g/L) was prepared in the reaction vessel and then bubbled with argon for 30 min to remove air. An alcohol was injected into the solution with a microsyringe through the septum just before irradiation. During the course of irradiation, the vessel was closed from the atmosphere.

In the analysis of the solutions, the sample was filtered through a membrane filter with a pore size of 0.2 $\mu$m to separate the $Al_2O_3$ powders. The absorption spectra of the solutions were measured by a spectrophotometer (Shimadzu UV-2100). The concentration of Pd(II) was determined by a colorimetric method with NaI; i.e., the absorption peak of $PdI_4^{2-}$ corresponding to Pd(II) was observed at 408 nm ($\epsilon$ = 9600 $M^{-1}$ $cm^{-1}$) by the addition of saturated NaI solution to the sample.[15,17] The acidity of the irradiated solution was measured by a pH meter (Horiba B-112). The separated powder was washed with distilled water and then analyzed. A transmission electron microscope (JEOL JEM-100S) and an X-ray diffraction instrument (Rigaku RINT-2200) were used in the characterization of the powder samples.

The catalytic activity of the sonochemically prepared $Pd/Al_2O_3$ was measured for the hydrogenation of olefins (1-hexene, *trans*-3-hexene) in a 1-propanol solution. Prior to the kinetic measurements, the catalysts were treated with $H_2$ gas at 200 °C for 2 h to remove any carbon and oxide species. In each experiment 0.16 mg of Pd was added to 1-propanol solution (30 mL) in a reaction vessel and kept at 1 atm of hydrogen for 60 min at room temperature before the reaction started. Then 1.18 mmol of olefin was introduced into the reaction system. Hydrogenation was carried out in a conventional closed system at 23 ± 0.5 °C under an initial $H_2$ pressure of 1 atm. The reaction rate was estimated from the amount of hydrogen uptake measured by a pressure gauge. A conventional Pd supported on $\alpha$-$Al_2O_3$ catalyst, which was prepared by $H_2$ reduction of impregnated Pd(II) at 200 °C for 2 h, was examined for comparison of the catalytic activity.

## Results and Discussion

**Sonochemical Reduction of Pd(II) Ions.** Figure 2 shows the changes in the concentration of Pd(II) during ultrasonic irradiation containing 2.02 g/L $Al_2O_3$ powders. This condition corresponds to the formation of 5 wt % $Pd/Al_2O_3$ (weight ratio of Pd to $Al_2O_3$), when the reduction of Pd(II) to metallic Pd is completed. The reduction of Pd(II) ions gradually proceeded in the presence of alcohol additives by ultrasonic irradiation. On the other hand, the reduction did not proceed

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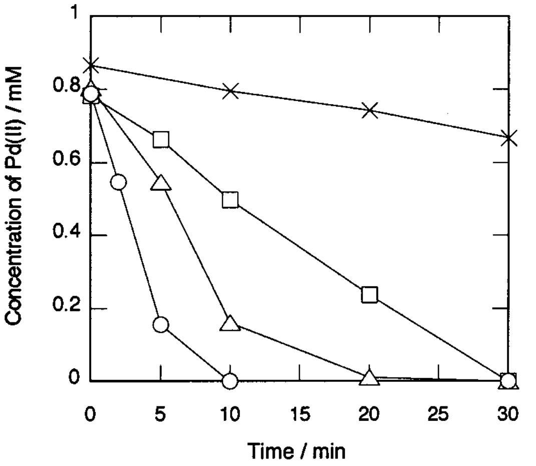

**Figure 2.** Changes in the concentration of Pd(II) during ultrasonic irradiation in the presence and absence of alcohol additives. Conditions: 2.02 g/L $Al_2O_3$, 20 mM alcohol. (×) None, (□) methanol, (△) ethanol, (○) 1-propanol.

without irradiation. These results suggested that hot-spot bubbles were sufficiently generated by irradiation even in a heterogeneous solution containing alumina powders so that the reduction successfully proceeded. The rates of reduction appreciably depended on the carbon number of alcohol additives; i.e., the rate increased in the order of methanol < ethanol < 1-propanol, although the same concentration of alcohol was present in the solution. The difference in the rate among these additives was considered to be attributed to the strength of hydrophobicity of alcohol additives as reported previously:[15,17] reducing radicals are more efficiently produced from higher hydrophobic compounds in water because the molecules can easily concentrate onto the interface of a hot-spot bubble at higher temperatures. This concentrating phenomenon of molecules is generally elucidated by the Gibbs adsorption equation dealing with an interface between a bulk solution and the gas phase. In the absence of alcohol, the change in the concentration of Pd(II) is also shown in Figure 2. The rate of Pd(II) reduction in pure water was extremely slow (7 μM/min) in comparison to those in the presence of alcohols.

The pH value of the sample solution remarkably decreased with irradiation time. The pH changes of the irradiated solution in the presence and absence of alcohol are presented in Figure 3. The decrease in the pH was presumably attributed to the progress of Pd(II) reduction to metallic Pd as shown in eqs 4−6.

$$H_2O \xrightarrow{)))} {}^{\bullet}OH + {}^{\bullet}H \qquad (1)$$

$$RHOH + {}^{\bullet}OH\ ({}^{\bullet}H) \rightarrow {}^{\bullet}R_{ab} + H_2O\ (H_2) \qquad (2)$$

$$RHOH \xrightarrow{)))} {}^{\bullet}R_{py} \qquad (3)$$

$$Pd(II) + {}^{\bullet}H \rightarrow Pd(I) + H^+ \qquad (4)$$

$$Pd(II) + {}^{\bullet}R_{ab}\ ({}^{\bullet}R_{py}) \rightarrow Pd(I) + R + H^+ \qquad (5)$$

$$Pd(I) + {}^{\bullet}H\ ({}^{\bullet}R_{ab}, {}^{\bullet}R_{py}) \rightarrow Pd(0) + R + H^+ \qquad (6)$$

where the mark ))) and RHOH denote a sonolysis and an alcohol additive, respectively. Equations 1−3 indicate

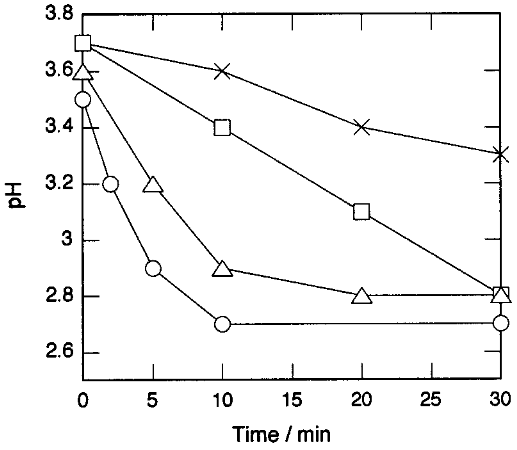

**Figure 3.** Changes in the pH of the sample solution during ultrasonic irradiation in the presence and absence of alcohol additives. Conditions: 1 mM Pd(II), 2.02 g/L $Al_2O_3$, 20 mM alcohol. (×) None, (□) methanol, (△) ethanol, (○) 1-propanol.

the sonochemical formation of various radicals[18,19] including the reducing radicals: (1) ${}^{\bullet}H$ is formed from water sonolysis, (2) ${}^{\bullet}R_{ab}$ is formed from the abstraction reaction of RHOH with ${}^{\bullet}OH$ or ${}^{\bullet}H$, and (3) ${}^{\bullet}R_{py}$ is formed via RHOH pyrolysis. Finally, the reduction of Pd(II) proceeds by the interaction with reducing radicals such as ${}^{\bullet}H$, ${}^{\bullet}R_{ab}$, and ${}^{\bullet}R_{py}$, as seen in eqs 4−6.[20] As an example similar to eq 5, it has been reported that the reduction of Ag(I) in the presence of 2-propanol proceeds as follows:[13]

$$(CH_3)_2CHOH + {}^{\bullet}OH \rightarrow (CH_3)_2\dot{C}OH + H_2O \qquad (7)$$

$$Ag(I) + (CH_3)_2\dot{C}OH \rightarrow Ag(0) + (CH_3)_2CO + H^+ \qquad (8)$$

The pH decrease in the presence of the alcohol additives paralleled the change in Pd(II) concentration, as shown in Figures 2 and 3. The $H^+$ ion concentration was, therefore, considered to increase according to the reduction of Pd(II) ions. As also shown in Figure 3, the pH value of the solution containing 1-propanol rapidly decreased from 3.5 to 2.7 in the initial 10 min irradiation, but no substantial change was observed upon further irradiation. The sonolysis of 1-propanol−water solution without Pd(II) was also carried out to confirm

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(20) The reduction of Pd(II) with H atoms in the presence of alcohol is almost negligible, because the rates of Pd(II) reduction were so much higher than that in pure water: the rate of reduction in the presence of 1-propanol was at least ca. 10-fold faster than that in pure water. Therefore, the reduction of Pd(II) in the presence of alcohol would mainly proceed by organic radicals generated in the sonolysis of an alcohol additive as seen in eqs 5 and 6. According to the previous report,[15] it was suggested that eq 6 would be a main reaction pathway in the presence of a hydrophobic compound. The fact that highly hydrophobic compounds can easily concentrate onto the interface of a bubble at high temperature was also reported by Grieser and co-workers[14b] and Henglein and co-workers [Henglein, A.; Kormann, C. *Int. J. Radiat. Biol.* **1985**, *48*, 251]. On the other hand, when methanol, a hydrophilic compound, was used as an organic additive, eq 5 would be a main reaction pathway because methanol molecules at low concentration could not sufficiently accumulate onto the interface of bubbles. This was supported by our experimental results that the rate of Pd(II) reduction in the presence of methanol (25 μM/min) almost corresponds to the combined rates of formation of H atoms and OH radicals, which were roughly estimated by the rate of formation of $H_2O_2$. The mechanism for the sonochemical reduction of Pd(II) was discussed in detail in ref 15.

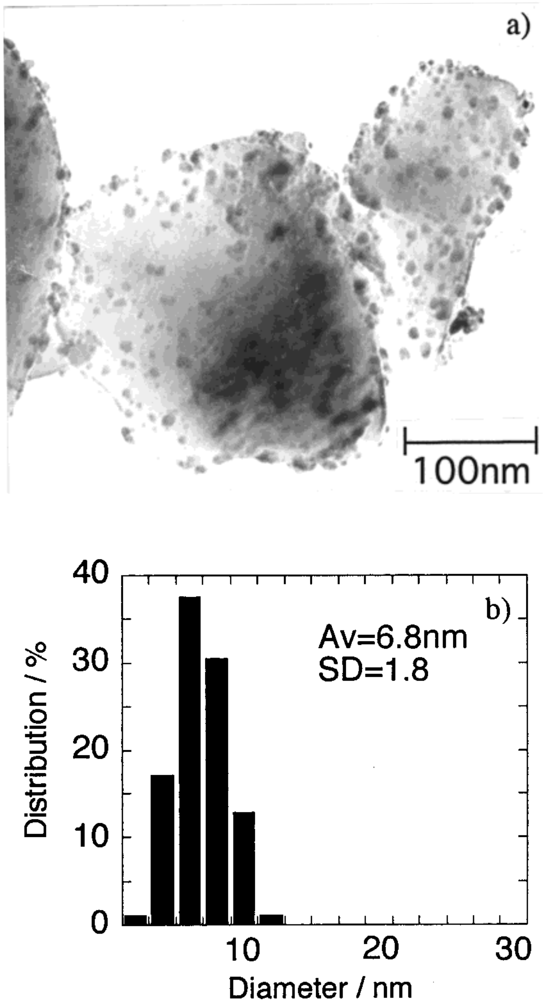

**Figure 4.** (a) TEM photograph and (b) size distribution of palladium particles of 1 wt % Pd/$Al_2O_3$, sonochemically prepared under Ar in the presence of 1-propanol. Conditions: 1 mM Pd(II), 20 mM 1-propanol, 10.5 g/L $Al_2O_3$, 30 min irradiation.

**Table 1. Average Size and Standard Deviation of Pd Particles Formed on the $Al_2O_3$ Surface and Rate of Pd(II) Reduction by Ultrasonic Irradiation[a]**

| conditions[b] | average size (nm) ± SD | rate[c] ($\mu$M/min) |
|---|---|---|
| 1 wt %, 1-propanol | 6.8 ± 1.8 | 120 |
| 1 wt %, ethanol | 7.4 ± 2.5 | 52 |
| 1 wt %, methanol | 7.9 ± 3.4 | 15 |
| 5 wt %, 1-propanol | 8.6 ± 2.8 | 130 |
| 5 wt %, ethanol | 10.0 ± 2.9 | 53 |
| 5 wt %, methanol | 11.3 ± 5.8 | 25 |

[a] 1 mM Pd(II), 20 mM alcohol, 30 min irradiation. [b] Weight ratio of Pd/$Al_2O_3$ and type of alcohol additive. [c] Average rate for initial 5min irradiation.

the relation between the Pd(II) reduction and the pH change. The sonolysis of 1-propanol−water solution exhibited a fairly small pH change as a function of irradiation time (changed from 5.7 to 5.2 in the 10 min irradiation), suggesting that the pH decrease in the presence of Pd(II) indicated the occurrence of Pd(II) reduction. This consideration was supported by the fact that the behavior of the pH change was in good agreement with that of Pd(II) reduction as shown in Figure 2. The progress of the reduction of Pd(II) to metallic Pd, therefore, can be monitored approximately by the measurement of the pH value of the solution.

**Analyses of the Resulting Powder.** The color of the $Al_2O_3$ powders gradually changed from white to black during the irradiation. The filtrate was a transparent solution without any colloidal dispersions. These observations suggest the formation of Pd particles on the surface of the $Al_2O_3$. The formation of metallic Pd was also confirmed by the X-ray diffraction pattern. No other distinct peaks attributed to PdO or other compounds of palladium were recognized in the reaction product. In addition, no appreciable formation of an amorphous phase was observed.

Figure 4 shows a transmission electron micrograph of the products in addition to the size distribution of the Pd particles on the $Al_2O_3$ powders. It was observed that spherical Pd particles were formed and they were homogeneously dispersed on the surface of the $Al_2O_3$ in a reasonably narrow range of size distribution compared with a conventionally prepared catalyst.[21] The average size and standard deviation of the Pd particles and the rate of Pd(II) reduction under several preparation conditions are summarized in Table 1. In this experiment, the initial concentrations of Pd(II), the concentration of alcohols, and the irradiation time were held constant at 1 mM, 20 mM, and 30 min, respectively.

As shown in Table 1, it was found that the size of the formed Pd particles and their distribution depended on the kinds of alcohol additives used. It might be concluded that the smaller particles could be obtained when the reduction of Pd(II) proceeded at the faster rate. Since an alcohol is an important additive for controlling the rate of Pd(II) reduction in the present sonication system, the size of Pd particles formed on the $Al_2O_3$ surface was considered to be easily controlled by choosing the appropriate alcohol. In addition, as the hydrophobicity of the alcohol increases, it is known to behave as a stabilizer for preventing the aggregation of colloidal particles, such as a surfactant. This implies that a more hydrophobic alcohol somewhat retards the growth of particles in an aqueous solution. Owing to the effects described above, the size of Pd particles decreased in the order of methanol > ethanol > 1-propanol. The standard deviation also decreased in the same order.

The effect of $Al_2O_3$ on the formation of Pd particles was investigated. The preparation of 1 and 5 wt % Pd/$Al_2O_3$ was carried out under these conditions: the initial concentration of Pd(II) ions and alcohol additive were maintained constant at 1 mM and 20 mM, respectively, with various amounts of coexisting $Al_2O_3$. The results are also indicated in Table 1. The size and the standard deviation of the Pd particles obtained became smaller when a larger amount of $Al_2O_3$ was present in the reaction system. Since the rate of reduction was almost the same between 1 and 5 wt % Pd/$Al_2O_3$ with the same alcohol additive, the rates of Pd nucleation were suggested to be almost equal to each other. Therefore, the growth and/or the agglomeration of the Pd particles in solution would be suppressed by the adsorption onto the $Al_2O_3$ surface so that the size of the formed Pd particles decreased with increasing amounts of $Al_2O_3$. In other words, the $Al_2O_3$ powder acts as a stabilizer for the Pd particles in the present sonication system.

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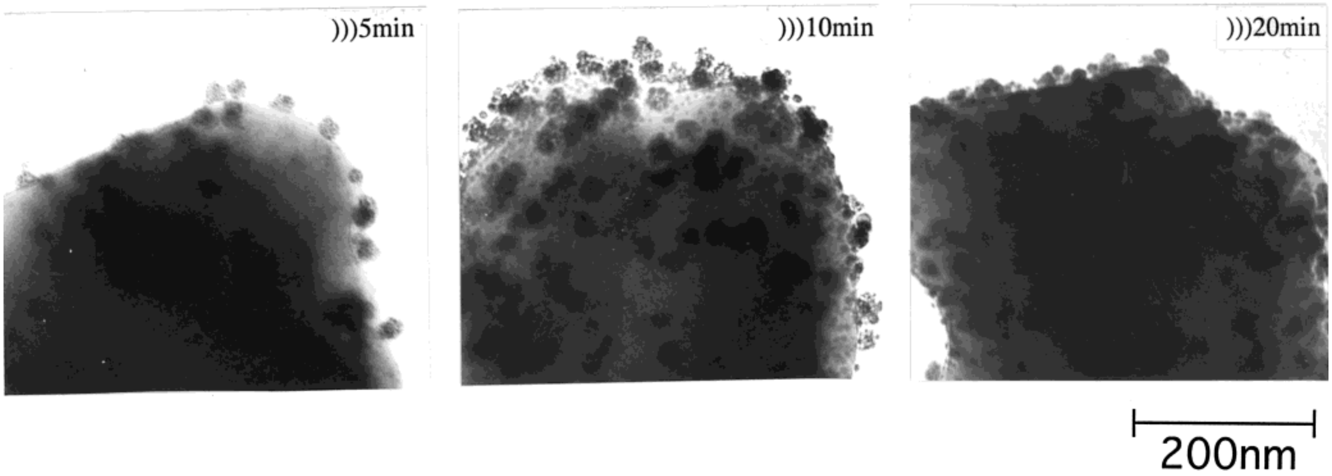
a) Methanol



b) 1-Propanol

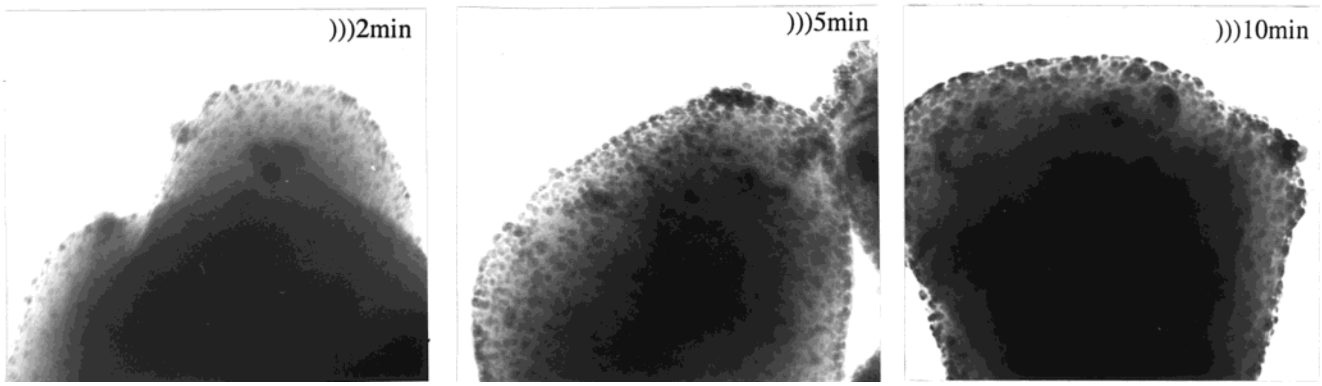


**Figure 5.** TEM photographs of sonochemically formed 5 wt % Pd/$Al_2O_3$, in the presence of (a) methanol and (b) 1-propanol during irradiation. Conditions: 1 mM Pd(II), 20 mM alcohol, 2.02 g/L $Al_2O_3$, Ar atmosphere.

To examine the formation processes of the supported materials, TEM observations of the resulting powder samples were carried out during the course of Pd(II) reduction. The results are represented in Figure 5. The TEM observation was performed for the sample prepared in the presence of 20 mM (a) methanol and (b) 1-propanol. On the basis of the results in Figure 2, the irradiation time was chosen so that the ratios of Pd(II) reduction were almost equal to each other. Prior to the irradiation, the clean and smooth surface of the $Al_2O_3$ was confirmed. It was observed that the number of the formed Pd particles depositing on the surface of the $Al_2O_3$ gradually increased as the reduction of Pd(II) proceeded. Distinct differences in the sizes of the Pd particles were recognized between the preparations in the presence of methanol and 1-propanol. In the case of methanol, relatively large particles were formed even in the initial stage, but the size was very small in the case of 1-propanol. The size of the Pd particles in both cases did not change during the course of irradiation. Further observations by TEM indicated that no substantial aggregation of Pd particles on the $Al_2O_3$ occurred by additional irradiation for 1 h, suggesting that no appreciable sintering of the Pd nanoparticles on the $Al_2O_3$ was recognized in the present 200 kHz sonication system.

It is well-known that ultrasonic cavitation provides various kinds of damage to materials due to such mechanical effects as shock waves, shear force, microjet, etc.[22] These effects have been practically applied in biology, medicine, and engineering.[7] In the field of colloid chemistry, ultrasound is one of the most common methods used to disperse or agglomerate colloidal material in solution. Although there were fears of the action of the mechanical effects on the Pd sintering in the present experiment, the sintering was rarely observed upon sufficient irradiation time. It has been reported, on the other hand, that the mechanical effects induced by ultrasound are considered to decrease with increasing ultrasonic frequency.[23] Since a relatively high frequency was used in the present sonication system, no substantial sintering would occur upon irradiation. Taking into account various physical effects of cavitation, it appears that high-frequency ultrasound should be applied for preparing nanostructured materials.

On the basis of the results obtained in the present experiments, the formation pathway of the supported materials is suggested as follows: the nucleation process (eq 6) and growth processes (eqs 9 and 10) of Pd nuclei occur in the bulk solution, and the immobilization (eq 11) of the Pd particles proceeds competitively toward its growth processes (eqs 9 and 10):

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$$\mathrm{Pd} \rightarrow\rightarrow \mathrm{Pd}_n \qquad (9)$$

$$\mathrm{Pd}_n \rightarrow\rightarrow \mathrm{Pd}_\mathrm{m} \qquad (10)$$

$$\mathrm{Pd}_n + \mathrm{Al_2O_3} \rightarrow \mathrm{Pd}_n \text{ immobilized on } \mathrm{Al_2O_3} \qquad (11)$$

where $Pd_n$ denotes Pd particles and $Pd_m$ a more aggregated, metallic species. Since the size of the particles is affected by the type of alcohol and the amount of $Al_2O_3$, it is clear that the growth of the Pd nuclei also occurs in the bulk solution. According to this proposed mechanism, it should be noted that the formed Pd particles are immobilized only on the surface of the $Al_2O_3$.

**Catalytic Activity of $Pd/Al_2O_3$.** The hydrogenation of olefins in a 1-propanol solution was employed to evaluate the catalytic activity of the sonochemically prepared $Pd/Al_2O_3$. Prior to the experiments it was confirmed that no appreciable reaction occurred in the absence of the catalyst. Figure 6 shows the amount of hydrogen uptake during the catalytic hydrogenation of 1-hexene. For comparison with the sonochemically prepared $Pd/Al_2O_3$, the results over a $Pd/Al_2O_3$ catalyst prepared by a conventional impregnation method and a commercially available Pd black catalyst are also shown in this figure. The initial rates of hydrogenation over the Pd black, the conventional $Pd/Al_2O_3$, and the catalysts sonochemically prepared in methanol and in 1-propanol were 30, 96, 320, and 700 $\mathrm{mmol\cdot(Pd\text{-}g)^{-1}\cdot min^{-1}}$, respectively. It is suggested that the activity of the present catalysts was 3−7 times higher than that of the conventionally prepared catalyst.

*Trans*-3-hexene, which has an internal C═C double bond, was used as another reactant to investigate the structure selectivity of the hydrogenation. The rates of the hydrogenation for olefins are summarized in Table 2. The hydrogenation of *trans*-3-hexene over the sonochemically prepared catalysts proceeded much faster than that over the conventional catalysts. The rate of *trans*-3-hexene hydrogenation was quite small in comparison with that of 1-hexene, indicating steric hindrance by the bulky groups adjacent to the C═C double bond in the molecules of *trans*-3-hexene. The ratio of the hydrogenation rate of 1-hexene to *trans*-3-hexene is also cited in Table 2. There was a tendency that the smaller the Pd size, the higher the ratio of 1-hexene to *trans*-3-hexene; i.e., the ratio decreased in the order catalyst sonochemically prepared in 1-propanol > catalyst sonochemically prepared in methanol > conventional catalyst > commercial Pd black. These obtained ratios would be affected not only by the different surface area of Pd metal particles but also because the reaction site of *trans*-3-hexene was different from that of 1-hexene or the Pd of the present catalysts would have other distinct properties such as an electric effect derived from the Pd size effect and an effect of strong metal−support interaction[24] of the $Al_2O_3$. Further detailed investigations are, of course, required to gain insight into the interaction between the catalytically active centers and the steric structures of reactant molecules.

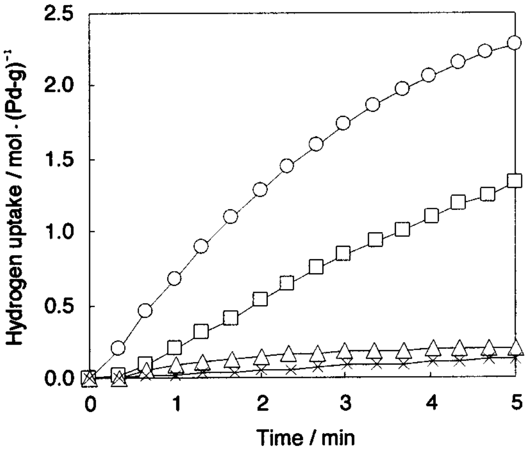

**Figure 6.** $H_2$ consumption in the hydrogenation of 1-hexene over various Pd catalysts. Conditions: 1 atm $H_2$, 23 ± 0.5 °C. (×) Pd black, (△) conventional $Pd/Al_2O_3$, (□) $Pd/Al_2O_3$ sonochemically prepared in methanol, (○) $Pd/Al_2O_3$ sonochemically prepared in 1-propanol.

**Table 2. Catalytic Activities of Pd Catalysts in the Hydrogenation of 1-Hexene and *trans*-3-Hexene**[a]

| | rate [$\mathrm{mmol\cdot(Pd\text{-}g)^{-1}\cdot min^{-1}}$] | | |
|---|---|---|---|
| catalyst | 1-hexene | 3-hexene | ratio[b] |
| 5 wt % $Pd/Al_2O_3$[c] | 700 | 70 | 10 |
| 5 wt % $Pd/Al_2O_3$[d] | 320 | 35 | 9.0 |
| 5 wt % $Pd/Al_2O_3$[e] | 96 | 14 | 6.9 |
| Pd black | 30 | 8.0 | 3.8 |

[a] Initial hydrogen pressure; 1 atm, temperature; 23 ± 0.5 °C. [b] 1-Hexene/3-hexene. [c] Sonochemically prepared in 1-propanol. [d] Sonochemically prepared in methanol. [e] Conventionally prepared.

## Conclusion

Highly dispersed Pd nanoparticles immobilized on $Al_2O_3$, having high catalytic activity in the hydrogenation of olefins, were prepared at room temperature by the sonochemical reduction of Pd(II) in an aqueous suspension. The reduction of Pd(II) under sonication could be monitored by measuring both the UV−vis spectra and pH of the irradiated solution. The size of formed Pd particles was easily controllable by selecting the type of alcohol additive and the amount of coexisting $Al_2O_3$. It is expected that the sizes of the Pd particles on $Al_2O_3$ could be more accurately controlled by selecting the types and concentrations of such organic additives as alcohols. The sonochemical reduction method appears to be a promising method in the preparation of supported materials.

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