Synthesis of Palladium Nanoparticles with Interstitial Carbon by Sonochemical Reduction of Tetrachloropalladate(II) in Aqueous Solution

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The metal particles of an interstitial solid solution of palladium carbide, PdC_x ($0 < x \le 0.15$), were synthesized at room temperature in aqueous solution during the reduction of tetrachloropalladate(II) with sonochemically produced organic radicals. The number of carbon atoms in the Pd particles were controlled by changing the concentration and the type of organic additives. The following mechanism of PdC formation is proposed: (i) an active Pd cluster is formed during the synthesis of Pd particles, (ii) organic additives are then adsorbed on the Pd cluster surface, and finally (iii) carbon atoms on the particle surface, which are formed from the catalytic dissociation of the additives, diffuse in the Pd metal lattice.
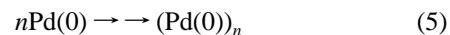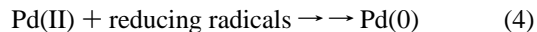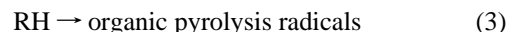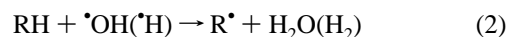
Various types of colloidal dispersions are now readily obtained by the reduction of the corresponding metal ions in solution or by the gas evaporation method,[1] and much attention has been paid to such colloidal dispersion of transition metal nanoparticles from the viewpoint of their application to catalysis.[1] The catalytic activity of the particles generally depends on their size,[2] shape,[3] and impurities,[4] which are controlled by the preparation conditions. Palladium is one of the most important catalytic materials that is used in various reactions in both industry and fundamental chemistry, so that its physical and chemical properties have been extensively investigated. It is well-known that palladium picks up hydrogen or boron atoms into its metallic lattice and undergoes phase transformations, which also leads to a change in its activity.[5]

Recently, the formation of palladium carbide, a metastable phase with carbon atoms on interstitial sites of a Pd metal lattice, PdC_x ($0 < x \le 0.15$), was reported, and its fundamental properties were examined. The PdC was formed by thermal treatment of supported Pd catalysts under an ethylene or acetylene atmosphere[6] or by an immediate contact of Pd clusters with acetone vapor,[7] and its structure was characterized by TEM and EXAFS.[7,8] The change in the catalytic activity due to the incorporation of carbon atoms, though implied,[9] has not yet been sufficiently clarified.

In this Letter we report on the formation of the PdC particles with various amounts of carbon (PdC_x: $0 \le x \le 0.15$) at room temperature by ultrasonic irradiation of an aqueous solution of tetrachloropalladate(II) (Pd(II)) in the presence of an organic additive. The control the amount of carbon in the lattice together with a proposal of the mechanism involved is discussed. Our experimental results suggest that the PdC phase may have been formed unintentionally by the conventional preparation methods of colloidal Pd metals and indicate that phase identification should be done carefully, considering the influence of the carbon uptake on the catalytic activity and/or surface chemistry of the particles.

Sonochemical reduction was carried out using a 200 kHz ultrasonic generator operating at 200 W (6 W/cm², 65 mm ∅). An aqueous solution of $PdCl_2 \cdot 2NaCl$ (1–10 mM, 60 mL) was placed in a cylindrical glass vessel (55 mm ∅), which had a silicon rubber septum for gas bubbling or sample extraction, without exposing the sample to air. The vessel was fixed at a constant position ($\lambda/2$: 3.75 mm above the oscillator) and then irradiated for 1 h under argon at 20 °C. The details of the irradiation setup are described in a previous paper.[10] Under our experimental conditions, the rate of formation of OH radicals and H atoms in the sonolysis of pure water was estimated to be 20 μM/min. An organic compound, which acts as an accelerator of the reduction of Pd(II), was injected into the solution using a microsyringe through the septum just before the irradiation.

Stable and fine colloidal Pd particles were obtained by the sonochemical reduction of Pd(II) in the presence of a suitable stabilizer such as a surfactant and a water-soluble polymer.[11] We have suggested that the reduction of Pd(II) and the formation of Pd metal particles proceed via the following equations

$$H_2O \rightarrow {}^{\bullet}OH + {}^{\bullet}H \tag{1}$$

$$RH + {}^{\bullet}OH({}^{\bullet}H) \rightarrow R^{\bullet} + H_2O(H_2) \tag{2}$$

$$RH \rightarrow \text{organic pyrolysis radicals} \tag{3}$$

$$Pd(II) + \text{reducing radicals} \rightarrow\ \rightarrow Pd(0) \tag{4}$$

$$n Pd(0) \rightarrow\ \rightarrow (Pd(0))_n \tag{5}$$

where RH denotes an organic additive, eqs 1–3 indicate the sonochemical formation of reducing radicals (${}^{\bullet}H$, $R^{\bullet}$, and organic pyrolysis radicals),[12] and eqs 4 and 5 indicate the reduction of Pd(II) and the formation of Pd metal particles,[11] respectively.

Figure 1 shows the X-ray diffraction (XRD) patterns of (a) standard Pd black (commercial) and (b) sonochemically prepared Pd metal particles from a 10 mM Pd(II) solution containing 100 mM of isopropyl alcohol. The pattern in (b) showed broad peaks corresponding to d spacing values of 2.29, 2.00, and 1.40 Å, which do not match the standard in (a) (d spacing values of 2.24, 1.94, and 1.37 Å). It should be noted that all of the peaks

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TABLE 1: Data of XRD Patterns of Pd Prepared by Sonochemical Reduction of Pd(II) in the Presence of Various Organic Compounds: 10 mM $PdCl_2$, 60 min Irradiation under Argon

sample	2θ (111)	2θ (200)	2θ (220)	PdC_x, $x =$	residual Pd(II) after sonication (mM)	rate of Pd(II) reduction (μM/min)
Pd black/100 mM isopropyl alcohol	40.05	45.5	68.10	0.03		
Pd(II)/100 mM methanol	40.23	46.7	68.36	0	4.1	100[b]
Pd(II)/100 mM ethanol	39.58	45.9	67.24	0.11	0	330[c]
Pd(II)/100 mM hexanol[a]	39.50	45.3	67.14	0.12	0	550[c]
Pd(II)/1 mM isopropyl alcohol	40.18	46.8	68.23	0.01	7.5	50[c]
Pd(II)/10 mM isopropyl alcohol	39.76	46.1	67.29	0.08	0	250[c]
Pd(II)/100 mM isopropyl alcohol	39.30	45.3	66.66	0.15	0	290[c]
Pd(II)/100 mM acetone	39.86	46.2	67.48	0.06	3.8	100[b]
Pd(II)/100 mM *tert*-butyl alcohol	39.30	45.4	66.80	0.15	4.4	93[b]

[a] Immiscible in water. [b] Average rate of reduction of Pd(II) for 60 min irradiation. [c] Initial rate of reduction of Pd(II); initial 5 min.
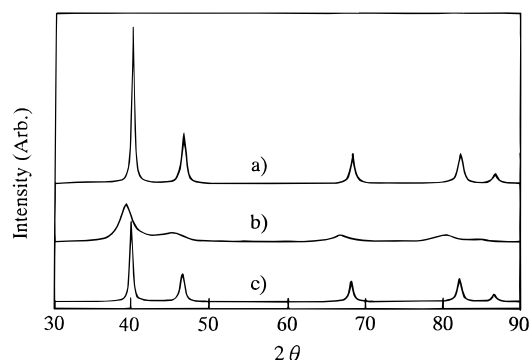

Figure 1. X-ray diffraction patterns (Cu-Kα1) of Pd metals: (a) standard Pd black, (b) sonochemically prepared Pd metal in the presence of isopropyl alcohol (c) annealed sample b in vacuum for 2 h at 600 °C. X-ray diffraction was done using a Rigaku RINT-1500 at 200 kV.

Figure 2. X-ray diffraction patterns (Cu-Kα1) of sonochemically prepared Pd metal in the presence of (a) methanol, (b) ethanol, (c) hexanol. Experimental conditions: $PdCl_2$, 10 mm; alcohol, 100 mM; irradiation time, 60 min.

in (b) are significantly shifted to a lower angle compared with those of standard Pd, indicating expansions of the Pd lattice in the face-centered cubic structure. The expansion cannot be explained in terms of hydrogen uptake, because hydride formation gives rise to a much greater expansion than that observed for the sonochemical preparation of Pd. Furthermore because the present sample was dried at 65 °C in an oven and stored in a desiccator under vacuum for one night before the XRD measurement, hydrogen incorporation is unlikely. Following the thermal treatment at 600 °C in vacuo for 2 h, the evolution of gas was observed and the sample exhibited the pattern in (c), in which all the peaks have become sharper and their locations are in good agreement with those of the standard Pd. No other peaks attributed to palladium oxide, palladium chloride, or other compounds of Pd were found. The XRD pattern observed here coincides with that previously reported on PdC.[6]

Elemental analysis of the sonochemically prepared Pd metal (sample b) showed it to be 98.2 wt % Pd, 1.7 wt % C, and 0.1 wt % H. Before the analysis, the sample was sufficiently washed with pure water and held under vacuum at 120 °C for 2 h to remove any trace amounts of adsorbates such as isopropyl alcohol and H_2O. The elemental analysis results clearly indicate the existence of carbon atoms in the Pd, and it was confirmed that an interstitial carbon:palladium of $PdC_{0.15}$ was formed under this condition.

In order to investigate the mechanism of PdC formation during sonication, an aqueous suspension of Pd black (63.8 mg/ 60 mL, corresponding to 10 mM Pd(II)) containing 100 mM of isopropyl alcohol was sonicated for 1 h. The XRD pattern of Pd black did not change upon the sonication, suggesting that various organic radicals, which were produced by the sonochemical decomposition of isopropyl alcohol, did not readily incorporate into the lattice of the Pd bulk state. Consequently,
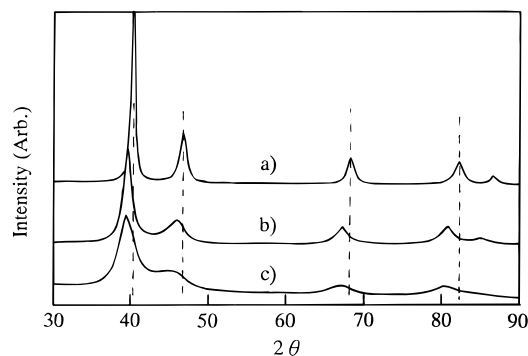
we assumed that there was an interaction between the Pd(II) ions or fine Pd clusters and the organic additive, and thus the formation of PdC probably occurred during the process of nucleation and/or growth of the Pd particles.
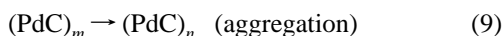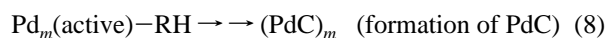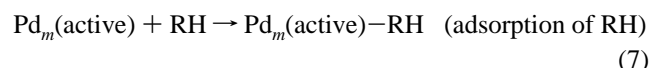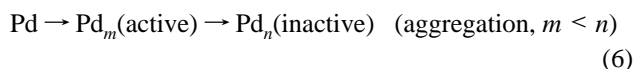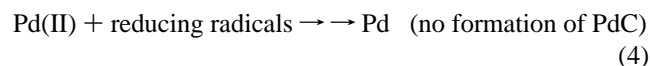
Figure 2 shows the XRD patterns of the Pd particles prepared in the presence of 100 mM of methanol, ethanol, and hexanol. The XRD data obtained under various experimental conditions are also summarized in Table 1. Different values of 2θ for each preparation condition were observed. Since the deviation in 2θ from the standard Pd was reflected by the amount of carbon in the Pd metal, we were able to estimate the composition of PdC as shown in Table 1. It was found that the carbon content in Pd was significantly affected by the type and the concentration of organic additives. In practice, it can be seen that as the carbon chain length in the additives is increased (methanol < ethanol < hexanol) and the concentration of isopropyl alcohol is higher, larger amounts of carbon atoms are contained in the Pd metal.

The rates of reduction of Pd(II) under our experimental conditions are also summarized in Table 1. From the comparison in the presence of methanol, acetone, and *tert*-butyl alcohol, the amount of carbon in the Pd particles was significantly diffrent, although the rates of reduction were almost equal to each other. This result indicates that the formation of PdC is not necessarily related to the rates of reduction. It was also clearly observed that the isopropyl alcohol concentration had a marked effect on the amount of carbon present in the particle (Table 1). This result suggests that PdC cannot be formed during the reduction process (Pd(II) → Pd(0)). The reason why is that the sonochemical reduction of Pd(II) assisted by isopropyl alcohol would proceed via the same reaction pathway at their different concentrations.[13] In addition, from the results of the comparison of Pd components in the presence of 10 mm isopropyl alcohol ($PdC_{0.07}$), 100 mM methanol (pure Pd), and 100 mM ethanol ($PdC_{0.1}$), it is proposed that the net amount of

carbon atoms in the reaction system (10 mM isopropyl alcohol < 100 mM methanol < 100 mM ethanol) is not closely related to the amount of the carbon atoms in the Pd particle.

From the results of Table 1, we suggest that the formation of PdC was affected by the nature of the organic additive, which is associated with their structure and functional groups.

It was reported that alkane molecules such as pentane and hexane were catalytically cleaved over Ni clusters under very low temperatures of about −130 °C because of their high catalytic activity.[14] More recently, the size dependence of transition metal clusters on their catalytic activity was observed in a gas phase reaction; small metal clusters consisting of several atoms to 20 atoms provided the highest activities for the activation of methane.[15] Consequently, we concluded that the fine Pd clusters would also be very reactive. If this was the case, the cleavage of an organic C−C or C−H bond would occur over the Pd clusters at room temperature. Thus, a possible mechanism of the formation of PdC is as follows: an active Pd cluster is formed during the process of the sonochemical formation of Pd particles (eq 6), an organic additive (RH) adsorbs on the surface of the Pd cluster (eq 7), and the dissociated carbon atoms, which form from the catalytic decomposition of RH, diffuse into the Pd lattice (eq 8).

$$Pd(II) + \text{reducing radicals} \rightarrow \rightarrow Pd \quad (\text{no formation of PdC}) \tag{4}$$

$$Pd \rightarrow Pd_m(\text{active}) \rightarrow Pd_n(\text{inactive}) \quad (\text{aggregation, } m < n) \tag{6}$$

$$Pd_m(\text{active}) + RH \rightarrow Pd_m(\text{active})-RH \quad (\text{adsorption of RH}) \tag{7}$$

$$Pd_m(\text{active})-RH \rightarrow \rightarrow (PdC)_m \quad (\text{formation of PdC}) \tag{8}$$

$$(PdC)_m \rightarrow (PdC)_n \quad (\text{aggregation}) \tag{9}$$

Using this proposed mechanism (the competitive reaction between eqs 6 and 7 exists), we can explain why various compositions in PdC are formed at the different concentrations of isopropyl alcohol.

We were able to directly synthesize the various components of the PdC particles in aqueous solution at room temperature. In addition, the carbon contents in the Pd metal were controlled by changing the type and the concentrations of the organic additives. From our experimental results, it is suggested that PdC is formed by the other preparation methods such as the alcohol reduction method,[16] gas evaporation method,[17] or method of reduction in water/oil emulsion system,[18] if sonochemical nucleation and/or growth process are the same as these methods. It is generally known that the surface properties and the catalytic activities of colloidal Pd particles are dependent on their preparation methods and conditions. Although there are many factors controlling the Pd activities, the formation of

PdC may lead to a change in the catalytic activities for a certain reaction that can be carried out under mild conditions below the limit of the thermal stability of the PdC phase.

We have presented the preliminary results for the formation of PdC particles in aqueous solution by ultrasonic irradiation. To clarify the detailed mechanism of PdC formation, an investigation of the effects of pH, ionic strength in solution, and addition of other types of organic additives is required.

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(9) Characteristics are (i) PdC phase does not decompose up to approximately 150 °C in a hydrogen or oxygen atmosphere (ref 6), that is, it is stable enough to allow many catalytic reactions in the colloidal state of PdC, (ii) the property of PdC drastically changes comparing with pure Pd as it loses ability to form PdH (ref 6), and (iii) most of the catalytic activities of metals can be improved by doping to enhance the stability toward inactivation or to control the catalytic selectivity (ref 4).

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