Structure and Catalytic Activities of Snolytically Prepared Noble Metal Nanoparticles

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Utilizing a cavitation phenomenon induced by irradiation of high-intensity ultrasound in an aqueous solution, gold(III), palladium(II), and platinum(IV) ions were reduced to Au(0), Pd(0) and Pt(0). Narrow particle size distributions could be obtained for those nanoparticles. The smallest particle size could be obtained for Pt(2-3nm) and Pd(5nm) in the sonolysis with polyethylene glycol monostearate. Metal cations were reduced by reducing radicals produced by the sonolytical decomposition of surfactant at high temperature interface between cavities and bulk solution. By irradiation of ultrasound to the aqueous solution of gold(III) and palladiumu(II) ions, gold(III) and platinum(IV or II) ions, and palladium(II) and platinum(IV or II) ions, nanosized gold/palladium, gold/platinum and palladium/platinum bimetallic particles could be obtained. The particles are found to be composed of core-shell, random alloy and the mixture of monometallic particles by a transmission electron microscopic and nanoarea energy-dispersive X-ray spectroscopic analyses. Bimetallic nanoparticles show higher activities for the hydrogenation of 4-pentenoic acid than for those of the mixture of nanometallic nanoparticles or random alloy with a corresponding bimetallic ratio.
Key words: nanoparticle, sonolysis, core-shell structure, random alloy, catalytic activity for hydrogenation

1. INTRODUCTION

The multifarious physicochemical properties of noble metal nanoparticles have attracted considerable attention in various fields of chemistry. High catalytic activities and selectivities and various interesting properties from a fundamental viewpoint have been reported.[1] There have been many studies on the methods for metal particle preparations, e.g., controlled chemical reduction,[2,3] photochemical or radiation-chemical reduction,[4,5] gas-evaporation,[6] and photocatalitic reduction.[7,8] We have studied the chemical effects of ultrasound and reported that colloidal noble metal particles can be prepared by ultrasonic irradiation of aqueous solutions of noble metal ions in the presence of surfactants.[9-12] This sonochemical method was applicable to the preparation of various types of noble metal nanoparticles such as bimetallic and supported ones.[13-17] It was found that colloidal Pd can be successively isolated from coexisting Pd ions without any morphological change by the treatment with an anion exchange resin. This makes possible the transmission electronmicrograph (TEM) obserbation and X ray diffraction pattern(XRD). In this paper, the formations and growth of Pd particles and bimetallic nanoparticles are investigated using the ion exchange method with an improved colorimetric method.[11]

2. EXPERIMENTAL

A cylindrical glass vessel was used for the ultrasonic irradiation, which had a side arm with a silicon rubber septum for gas bubbling or sample extraction without exposing the solution to air. During the irradiation, the vessel was closed. A multiwave ultrasonic generator and a barium titanate were used for the sonication and operated at 200kHz with an input power of $6W/cm^2$. TEM specimens were prepared by placing droplets of the sample onto a carbon film supported on a copper grid and drying in a vacuum. Specimens for XRD measurement were prepared by adding NaCl to the colloidal dispersion to form aggregations, which were filtered out, rinsed and dried in vacuum. An argon equilibrated 25 mL of aqueous Na_2PdCl_4 solution (1mM) containing a surfactant sodium dodecyl sulfate (SDS) was sonolyzed in a glass reaction vessel. The formation of metallic Pd was also confirmed by its XRD pattern (Cu Kα1): a diffraction peak at 2h = 39.3 (*d* spacing of 2.29Å) corresponding to the (111) plane of elemental Pd.

3. RESULTS AND DISCUSSION

As sown in Tables 1 and 2, by irradiation of ultrasound to the

aqueous solution of gold(III) and palladiumu(II) ions, gold(III) and platinum(IV or II) ions, and palladium(II) and platinum(IV or II) ions, nanosized gold/palladium, gold/platinum and palladium/platinum bimetallic particles could be obtained and those are found to be composed of core-shell, random alloy and the mixture of monometallic particles by a transmission electron microscopic and nanoarea energy-dispersive X-ray spectro- scopic analyses. The color of the solution changed from an initial pale yellow to dark brown with the irradiation and the photo-absorption peak at about 300 and 400 nm characteristic of Pd (II) decreased while a broad absorption band from the UV to the visible region assigned to Pd particles appeared. Fig. 1 shows the photoabsorption spectra of 90 s irradiated sample (24% progress of reaction) before and after ion-exchange resin treatment. The absorption due to Pd(II) ions disappears and only the spectrum of the remaining Pd particles is present, indicating that the Pd colloids and ions can be readily separated by this method. Fig.2 and Table 3 respectively show a TEM photograph and various data for the Pd particles at

different irradiation times. It was observed that the size of the Pd particles became larger with sonication time, but their number remained approximately constant. The chemical effects of ultrasound are attributed to cavitation which is accompanied by conditions of high temperature and high pressure. In aqueous sonochemistry, three different reaction sites have been postulated.

a)Interiors of collapsing cavities where temperatures of several thousand degrees and pressures of hundreds of atmospheres have been reported to exist.[18] Water vapor is pyrolyzed to OH radicals and hydrogen atoms,[19,20] and gas-phase pyrolysis and/or combustion reactions[21,22] of volatile substances dissolved in water take place.

b)Interfacial regions between the cavitation bubbles and the bulk solution at ambient temperature with a high temperature gradient is still present in this region.[23] Locally condensed OH radicals in this region have been reported.[24]

c)Bulk solution at ambient temperature where reactions of OH radicals or hydrogen atoms take place.

Table 1   EDX analytical results of Au/Pd core-shell nanoparticles

	(a)Au/Pd=1/1			(b)Au/Pd=1/4		
	whole	center	edge	whole	center	edge
Au(atom%)	49.6	76.0	3.6	24.9	55.8	0.7
Pd(atom%)	50.4	24.0	96.4	75.1	44.2	99.3

Table 2   Structures of the sonolytically prepared bimetallic nanoparticles

Noble metal ions	Surfactants	Structure of nanoparticles
Au(III)/Pd(II)	SDS	core-shell
	PEG-MS	random alloy
Au(III)/Pt(IV)	SDS	mixture of monometallic particles
	PEG-MS	core-shell
Pt(IV)/Pd(II)	SDS	random alloy

Table 3. Palladium particles at various irradiation time

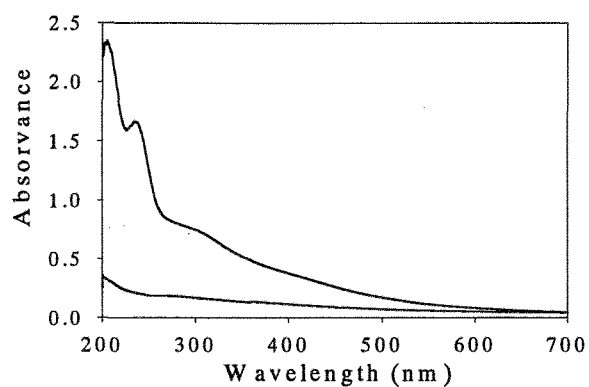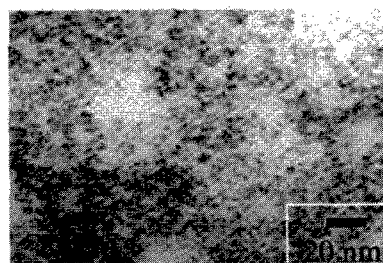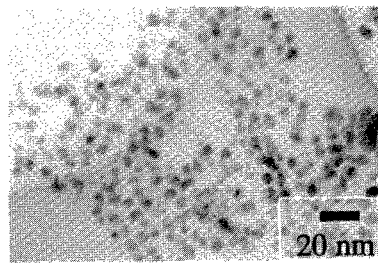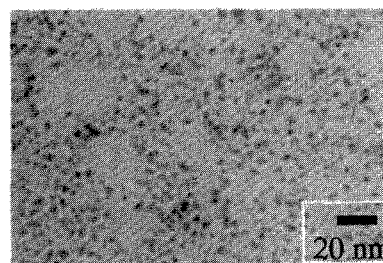| Irradiation time (min)	Progress of reaction (%)	Size (nm)	Numbers of particles
0.5	9	3.2±1.4	3.0×10^{16}
1.5	24	4.2±2.2	2.7×10^{16}
3	36	5.6±1.1	3.0×10^{16}
6	78	6.0±3.4	3.1×10^{16}
15	100	7.0±3.2	3.0×10^{16}
75	100	6.6±2.2	4.2×10^{16}

Fig.1. Photoabsorption spectra of 90 s sonicated solution
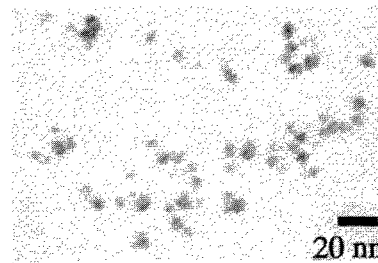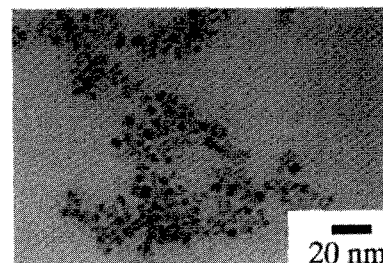(a) before and (b) after treatment with anion-exchange resin.
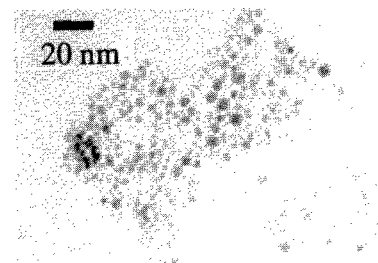(Pd(II) 1 mM, SDS 8mM)
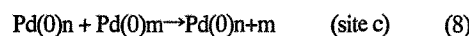

(a) 30s sonication
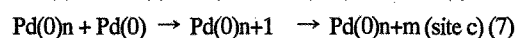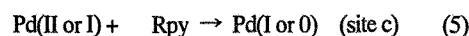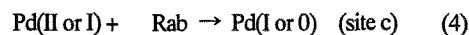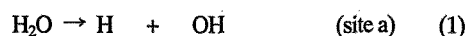
(d) 6 min

(b) 1.5 min

(e) 15 min

(c) 3 min

(f) 75 min

Fig.2. TEM photograph of Pd particles at various reduction stages.
(Pd(II) 1 mM, SDS 8 mM)

In the present reaction system, the following equations are proposed to explain the generation of the reducing species, the reduction of ions, and nucleation and growth of Pd particles

$$H_2O \rightarrow H + OH \qquad\qquad \text{(site a)} \qquad (1)$$
$$R + OH(H) \rightarrow Rab \qquad \text{(site b and c)} \qquad (2)$$
$$R \rightarrow Rpy \qquad\qquad\qquad \text{(site b)} \qquad (3)$$
$$Pd(II \text{ or } I) + \quad Rab \rightarrow Pd(I \text{ or } 0) \quad \text{(site c)} \qquad (4)$$
$$Pd(II \text{ or } I) + \quad Rpy \rightarrow Pd(I \text{ or } 0) \quad \text{(site c)} \qquad (5)$$
$$nPd(0) \rightarrow Pd(0)n \quad \text{(nucleation)} \quad \text{(site c)} \qquad (6)$$
$$Pd(0)n + Pd(0) \rightarrow Pd(0)n{+}1 \rightarrow Pd(0)n{+}m \text{ (site c)} \ (7)$$
$$Pd(0)n + Pd(0)m \rightarrow Pd(0)n{+}m \qquad \text{(site c)} \qquad (8)$$

where R denotes SDS.

Reaction 2 (mainly hydrogen abstraction) would proceed at the interface and in the bulk solution. Reaction 3 indicates the formation of reducing radicals via pyrolysis of SDS at the interface and this would be the main pathway of reducing radical formation considering the rate of formation of OH radicals (19 mM/min) and that of reduction of Pd(II) ions to Pd(0) (180 mM/min). The surfactants appear to concentrate at the interface[25] and sufficiently supply the reducing radicals by pyrolysis. Reactions 4-8 would mainly occur in the bulk solution because hydrophobic Pd ions may be uniformly dispersed around the interface and the bulk solution, and the bulk solution makes up the overwhelming quantity of the reaction site. The growth would proceed via reaction 7 (Pd (0) is combined to nucleate Pd clusters) and the role of reaction 7 (combination between the clusters) seems to be little.

4. ACKNOWLEDGEMENT

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