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Sonolytical Preparation of Nanoparticles of Noble Metals

Yasuaki MAEDA[a], Yoshiteru MIZUKOSHI[a], Eiji TAKAGI[a], Taku FUJIMOTO[b], Ryuichiro OSHIMA[b], and Yoshio NAGATA[b]

[a] Department of Applied Materials Science, College of Engineering, Osaka Prefecture University 1-1 Gakuencho Sakai 599-8531, Japan, e-mail: maeda@ams.osakafu-u.ac.jp

[b] Res.Inst. for Advanced Sci. and Technol.,Osaka Prefecture University

Sonolytical preparation of nanoparticles of Au, Ag, Pt, Pd has been studied in aqueous phase. In the presence of surfactant, noble metal cations were rapidly reduced to metal to produce nanoparticles. 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 radical produced by the sonolytical decomposition of surfactant at high temperature interface between cavities and bulk solution. Rates of the reduction of metal cations in the presence of SDS were Pd(II):130(μM/min), Au(III):83, Pt(II):19, Ag(I):7, respectively. Those rates were faster than those by γ-ray irradiation which were Pd(II):34, Au(III):11, Pt(II):10, respectively. Palladium nanoparticles with interstitial carbon could be obtained in the sonolysis with alcohol. Pt(IV) ion is consecutively reduced to zero valent metal in two steps: step (1):Pt(IV)ion to Pt(II)ion, and step (2):Pt(II) ion to Pt(0) In the sonolysis of aqueous solutions of SDS, DBS or PEG-MS, two kinds of organic reducing radicals (Rab and Rpy) are proposed to contribute the reduction. Radical Rab is formed from hydrogen abstraction of OH radical from surfactants. Rpy is formed from the direct thermal decomposition of surfactants in the interfacial region. Rab is effective for the both reduction steps(I) and(II), while Rpy is involved only in the reduction step (1).

Key Words: Nanoparticles, noble metal, sonolytical reduction, surfactants, catalyst

1.INTRODUCTION

Nanoparticles of noble metals have attracted special attention in various fields of chemistry since they have high catalytic activities and selectivities.[1-3]And many methods have been developed for the preparation of metal particles such as reduction by chemical reductants [4,5], photochemical or radiative reduction [6,7] , gas evaporation [8,9].The sonolytical method has also been developed for the preparation of nano-particles of noble metal[10-12]. In this paper, we report the role of surfactants for the sonolytical preparation of nanoparticles of noble metals in aqueous phase.

2.EXPERIMENT

Ultrasonic irradiation was carried out by using a multiwave ultrasound generator with a barium titanate oscillator of 65mm diameter (Kaijo 4021, 200kHz, 6w/cm^2) as shown in Fig.1. The argon-purged aqueous solution of noble metal ions in the presence of surfactants was sonicated. During the sonication the vessel was closed to prevent the contamination of air. γ Irradiation was performen under N_2O atmosphere with dose rate of 2.5kGyh^{-1} which provide the same formation rate of hydroxyl radical as in sonolysis. All chemicals purchased from Wako Chemicals were reagent-grade and used without further purification.

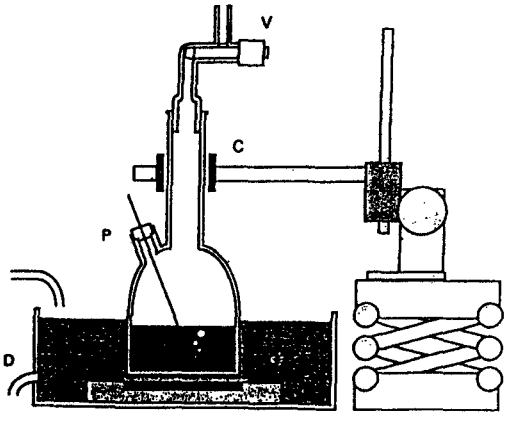


Fig.1 Irradiation apparatus
V:valve, C:clamp, P:septum, I:water inlet, S:sample solution, O:oscillator, D:water outlet

3.RESULTS AND DISCUSSION

As shown in Fig.2, Pd(II) ions were rapidly reduced to monometallic nanoparticles during the sonication. Au(III), Pt(II) and Ag(I) were also reduced to nanoparticles with different reduction

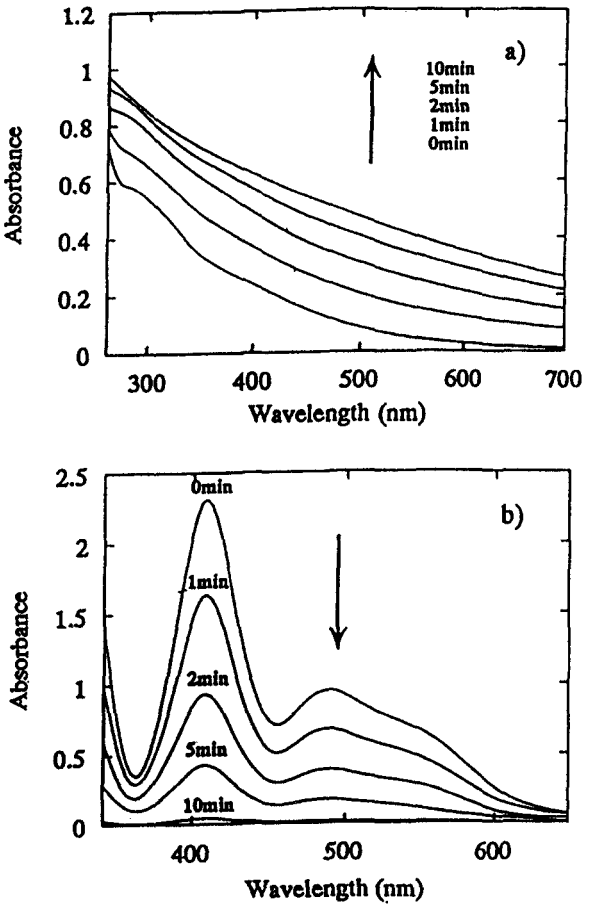


Fig.2 Absorption spectra of a) iiradiated Pd(II) in SDS solution, b) after addition of NaI solution to a). Pd(II): 0.5mM, SDS: 8mM, Cell length: 0.5cm

rates as shown in Table 1. These rates did not reflect the redox potential of each metal cations. 0.62V=$[PdCl_4]^{2-}$,1.002V=$[AuCl_4]$ 0.758V=$[PtCl_4]^{2-}$, 0.799V=$[Ag^+]$. The reduction rate was slow without surfactant, however reduction rate were accelerated in the presence of surfactants as shown in Fig.3. As shown in Fig.4, nanoparticles prepared by sonolytical reduction have nallow size distribution. Comparing with sonolysis the reduction rate of γ ray irradiation was slow and irregular in size as shown in Fig.5 and Table2.

Table 1 Reduction rates of noble metal ions

Sample	Rate of ultrasonic irradiation under Ar (μM/min)		Rate of γ-ray irradiation[b] under N_2O (μM/min)
	None	SDS[a]	SDS
Pd(II)	4	130	34
Au(III)	4	83	11
Pt(II)		19	10
Ag(I)	~0	7	

[a]SDS, 8 mM.
[b]Dose rate 2 kGy/h: under these conditions, the rate of formation of OH radicals is 20 μM/min.

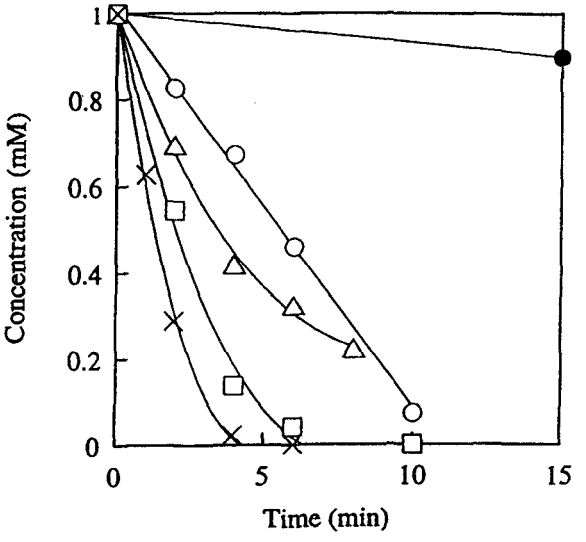


Fig.3 Reduction of Pd(II) under argon by ultrasonic irradiation in the presence of various stabilizer. Initial concentration of Pd(II): 1mM, (●); none, (△); SDS, (□); PEG-MS, (×); Tween20. (○); PVP,

Sonochemical reduction processes of Pt(IV) ions in water have been investigated in the presence of various kinds of surfactants such as sodium dodecylsulfate (SDS) and sodium dodecyl-benzenesulfonate (DBS) as anionic surfactants, and polyethlene-glycol monostearate (PEG-MS) as non-ionic, dodecyltrimethyl-anmmonium chloride (DTAC) and bromide (DTAB) as cationic surfactants to elucidate the role of surfactants in the sonolytical reduction. The determination of Pt(IV) ,Pt(II) and Pt(0) in the sonicated sample

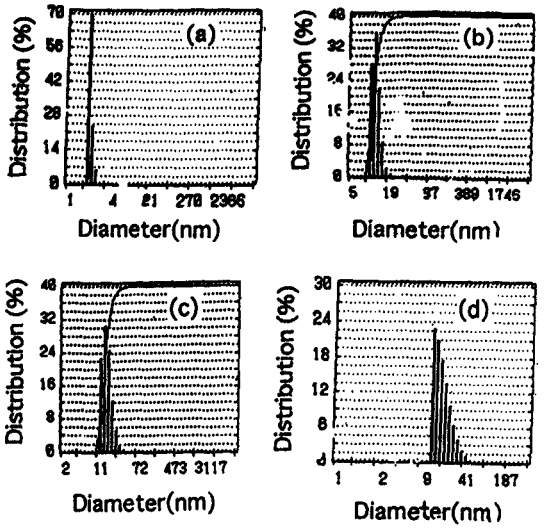


Fig.4 Size distribution of metal particles irradiated under Ar, (a)Pt, (b)Ag, (c)Au, (d)Pd

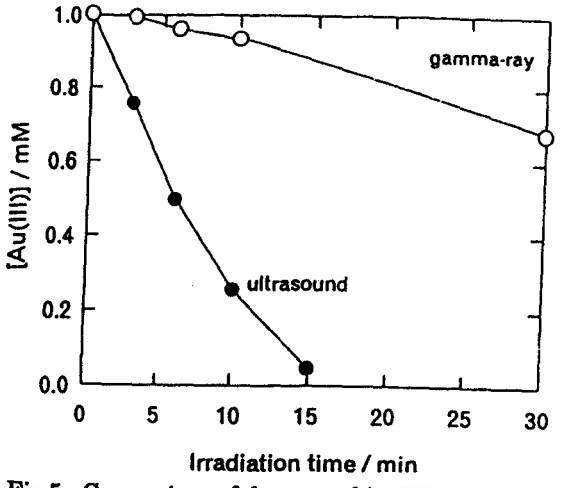
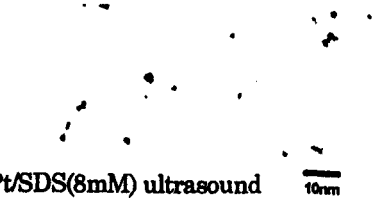


Fig.5-aComparison of the rate of Au(III) reduction by γ ray and ultrasound, dose rate 2.5x10⁶R/h



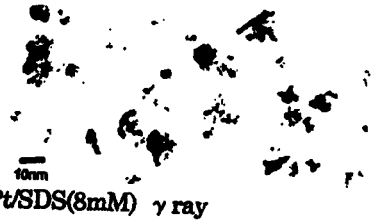
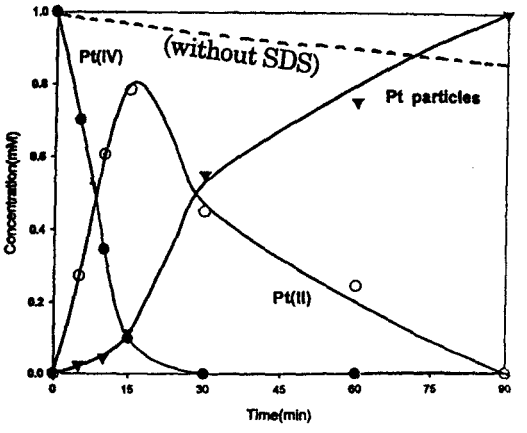


Fig.5-b TEM image of particles

Table 2 Particle size controll

Initial conc. of Pd(II) (mM)	Stabilizer	Size (nm)
0.1	SDS	8.4
0.5	SDS	9.5
0.75	SDS	10
1.0	SDS	88
1.0	PVP	110
1.0	PEG-MS	14
1.0	Tween20	5.3

solution shows that the reduction of Pt(IV) proceeds stepwise via divalent ionic species with the reduction rate of each steps, from Pt(IV) to Pt(II) and Pt(II) to Pt(0) to be 96 and 24 μ M min^{-1}, as shown in Fig.6. This result shows that even in the presence of different kind of surfactants, reduction of Pt(II) proceeds at the same rate of 20 μ M min^{-1} which is the same as the formation rate of OH radical in the sonolysis of aqueous solutions. Furthermore, the reduction in the γ ray irradiation,



Pt(IV)→ Pt(II) 96 μMmin^{-1}

Pt(II) → Pt(0) 24 μMmin^{-1}

(H_2PtCl_6; 1 mM,SDS; 8 mM,under Ar)

Fig.6-a Time profile of Pt(IV), Pt(II) and Pt(0).

which is well kown as the process to produce OH radical, reduction rates of Pt(IV) and Pt(II) were 20 μ Mmin^{-1}. From these facts we conclude that two kinds of organic reducing radicals (Rab and Rpy) are proposed to contribute the reduction. Radical Rab is formed from hydrogen abstraction of OH radical from surfactants.

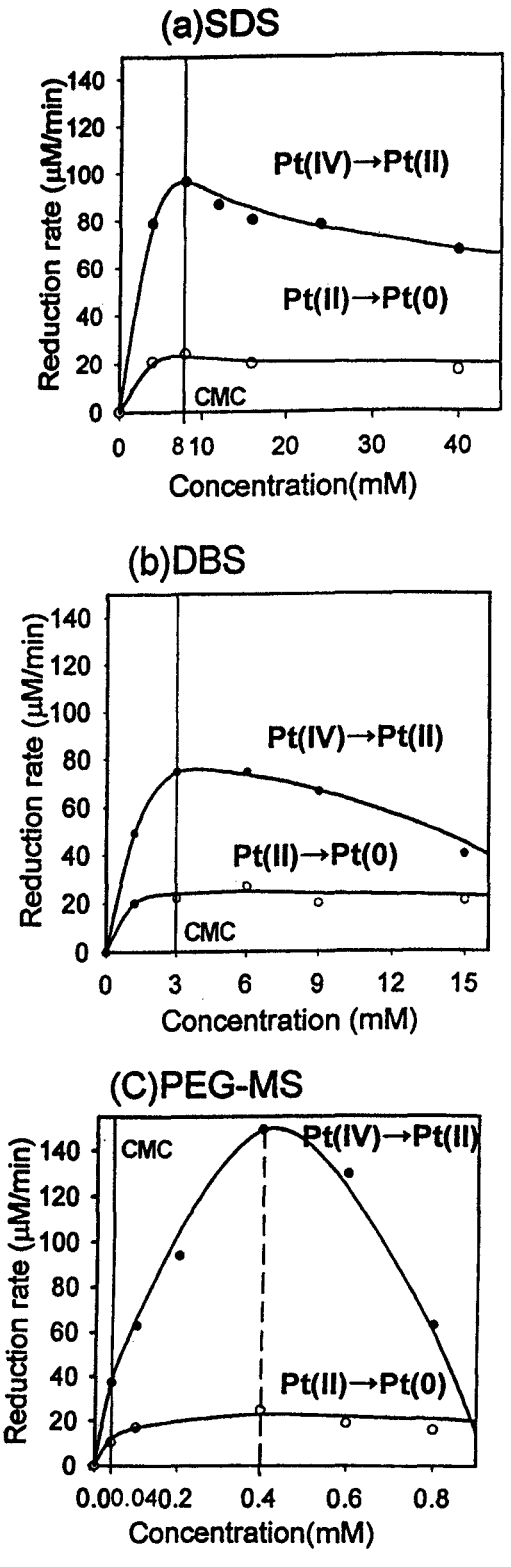


Fig.6-b Effects of surfactants on the reduction of Pt(IV) and Pt(II).

Rpy is formed from the direct thermal decomposition of surfactants in the interfacial region between the collapsing cavities and the bulk water. Rab is effective for the both reduction steps(I) and(II), while Rpy is involved only in the reduction step (I). This fact coincides with the previously reported sonochemical reducation of Pt(II) ions[13]. Hydrogen atoms themselves, which are produced from the pyrolysis of water, scarcely participate in the reduction of noble metals. The average diameter (1.0 nm) of platinum particles from the system of PEG-MS is smaller than those from the aqueous solution of anionic surfactant SDS(3.0 nm) and DBS(3.0 nm).

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5. AKNOWLEDGEMENT

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