

Formation of noble metal particles by ultrasonic irradiation

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Abstract

It was found that sonochemically prepared metal particles such as Ag, Pd, Au, Pt and Rh are of nanometer size with a fairly narrow distribution (e.g., about 5 nm for Pd particles obtained from a 1.0 mM Pd(II) in polyethylene glycol monostearate solution). We have suggested three different reduction pathways under sonication: (i) reduction by H atoms, (ii) reduction by secondary reducing radicals formed by hydrogen abstraction from organic additives with OH radicals and H atoms, (iii) reduction by radicals formed from pyrolysis of the additives at the interfacial region between cavitation bubbles and the bulk solution. The reduction of Ag(I) and Pt(II) mainly proceeds through reaction pathway (ii). In the cases of Pd(II) and Au(III), the reductions mainly proceed through reaction pathway (iii). The reduction of Rh(III) was not achieved under the same conditions; however, by the addition of sodium formate, reduction occurred and the preparation of Rh particles succeeded.

Keywords: Noble metal particles; Sonochemical reduction; Cavitation

1. Introduction

Nano-size particles of noble metals have attracted considerable attention in various fields of chemistry because of their conspicuous physicochemical properties. Therefore, it is of interest to develop an effective preparation method for these particles. Ultrasonic irradiation of liquids is known to provide various chemical and physical effects [1]. However, most of the chemical reactions induced by ultrasonic irradiation in aqueous solution are oxidations; there are only a few preliminary investigations of the reduction of noble metal ions [2,3]. We study the sonochemical reduction of noble metal ions and the preparation of ultrafine particles



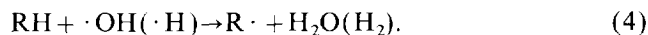
It was found that stable and fine particles of Ag [4], Pd [5], Au [6], Pt and Rh are sonochemically produced from aqueous solutions of the corresponding metal ions in the presence of a stabilizer (RH), such as a surfactant or a water-soluble polymer, and the sizes of the particles are of nanometer order. It was also found that the

stabilizers are a source of reducing radicals under sonication conditions. We have suggested that there are three reduction pathways via three types of reducing radicals under sonication in the absence and presence of RH.

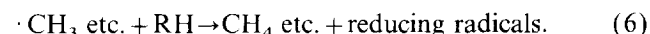
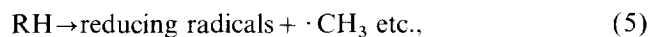
Reduction (i) (reduction by H atoms formed from water sonolysis)



Reduction (ii) (reduction by secondary reducing radicals, $R\cdot$, which are formed by hydrogen abstraction from RH with OH radicals and H atoms)



Reduction (iii) (reduction by reducing radicals formed via pyrolysis of RH at the interfacial region between the cavitation bubbles and the bulk solution)



In this paper, we report the sonochemical reduction mechanism for noble metal ions, the roles of the organic additives, and the properties of the particles prepared by sonication.

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2. Experimental

The sonolysis was carried out according to the same experimental procedure described previously [5]. A 60 ml sample solution of AgNO₃, PdCl₂·2NaCl, NaAuCl₄, K₂PtCl₄ or RhCl₃ (0.1–1.0 mM) was placed in a cylindrical glass vessel (55 mm Ø) which had a silicone rubber septum for gas bubbling or sample extraction, without exposing the sample to air. Ultrasonic irradiation was performed using a 200 kHz generator (6 W/cm², 65 mm Ø) under argon at 20°C. 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. Nonionic surfactants (polyoxyethylenesorbitan monolaurate, Tween20; polyethylene glycol monostearate, PEG), an anionic surfactant (sodium dodecylsulfate, SDS) or a water-soluble polymer (polyvinylpyrrolidone, PVP) were used as the stabilizers for colloidal particles. The concentration of metal ions in the irradiated solution was measured with the improved colorimetric method [7]; NaI was added as a color-producing reagent for Pt(II).

3. Results and discussion

When the sample solution containing noble metal ions and a stabilizer was irradiated, the color of the solution changed to that characteristic of each metal and the scattering of light from a He–Ne laser was observed. For example, the color of Pt(II)–SDS solution changed from pale yellow to brownish black on ultrasonic irradiation and, at the same time, a broad absorption band from the UV to the visible region assigned to platinum particles appeared. The formation of Pt metal particles was confirmed by the X-ray diffraction pattern.

Table 1 shows the rates of reduction of various metal ions in the absence and presence of SDS by irradiation.

Table 1

Initial rates of reduction of noble metallic ions in the absence and presence of SDS by ultrasonic irradiation and γ-ray irradiation

Sample	Rate of ultrasonic irradiation under Ar (µM/min)		Rate of γ-ray irradiation ^b under N ₂ O (µM/min)
	None	SDS ^a	
Pd(II)	4	130	34
Au(III)	4	83	11
Pt(II)		19	10
Ag(I)	~0	7	

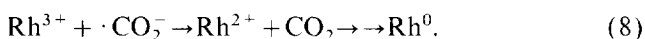
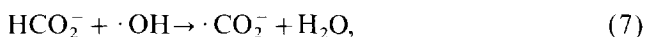
^aSDS, 8 mM.

^bDose rate 2 kGy/h; under these conditions, the rate of formation of OH radicals is 20 µM/min.

The rates of sonochemical reduction in the presence of SDS were in the order Pd(II) > Au(III) > Pt(II) > Ag(I), and it was observed that the rates of reduction of Pd(II) and Au(III) in SDS solution were much higher than in pure water. We have suggested [5,6] that the increase in the rates could be attributed to reducing radicals produced by pyrolysis of SDS and the reduction of Pd(II) and Au(III) mainly proceeding via reduction (iii).

The rate of reduction of Pt(II) was considerably slower compared with those of Pd(II) and Au(III). For comparison with sonochemical reduction, the rates of reduction by γ-ray irradiation under N₂O are also shown in Table 1. The radiolytic reduction under N₂O proceeds by the reaction of H atoms and by the reaction of secondary reducing radicals, R·, which are produced by OH radicals and H atoms abstraction from RH. From the results of both the sonochemical reduction and the radiolytic reduction of Pt(II), the reduction of Pt(II) under sonication would proceed via reduction (ii) rather than reduction (iii) as would the reduction of Ag(I), taking into account the high concentration of SDS and OH radicals at the interfacial region [8].

It is generally known that the redox potentials for these noble metal ions are exceedingly high, therefore the reduction by reducing radicals should occur readily. In fact, the reduction by sonication proceeded easily, however the order of the rates (Pd(II) > Au(III) > Pt(II) > Ag(I)) did not reflect the redox potential of each of the metal ions ([PdCl₄]²⁻, 0.62 V; [AuCl₄]⁻, 1.002 V; [PtCl₄]²⁻, 0.758 V; Ag⁺, 0.799 V at 25°C). The details of the reduction mechanism have not been clarified, so we investigated the factors influencing the rates of reduction under sonication. Attempts at producing the reduction of Rh(III) by the same procedure were unsuccessful, although the redox potential of Rh(III) is 0.758 V, the same as that of Pt(II). However, Rh(III) reduction succeeded by transforming OH radicals into highly reducing radicals, ·CO₂⁻, by the addition of sodium formate which is known to form highly reducing radicals:



We expect that it is possible to reduce metal ions having a higher redox potential than ·CO₂⁻ which can easily be produced by adding sodium formate.

The sizes of the noble metal particles produced by the sonochemical reduction method were very fine and very stable in the colloidal state. The stabilities of platinum particles prepared under various conditions are listed in Table 2. The particles prepared in the absence of stabilizer were unstable and aggregated within several hours. On the other hand, in the presence

Table 2
Stabilities of platinum particles prepared by sonication under argon

Sample (1 mM)	Stabilizer	State of reduced metal
K ₂ PtCl ₄	PEG-MS (0.4 mM)	Colloid ^a
	Tween20 (5 g/l)	Colloid
	SDS (8 mM)	Colloid
	PVP (1 g/l, <i>M_w</i> 40 000)	Colloid-ppt ^b
	None	Ppt ^c

^aColloid: stable more than a few months.

^bColloid-ppt: precipitation after a week.

^cPpt: precipitation after several hours.

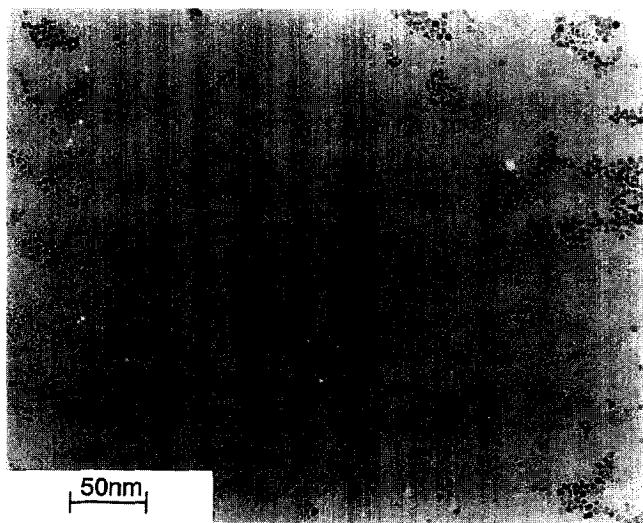


Fig. 1. Transmission electron micrograph of palladium particles prepared by the sonochemical reduction method.

of stabilizers, most of the particles were stabilized and persisted for several months in the colloidal state.

Fig. 1 shows as an example a transmission electron micrograph of palladium particles prepared from a solution of 1.0 mM Pd(II) in the presence of PEG. The average size of the particles is about 5 nm and has a narrow distribution over a small range. Similar results were obtained in the preparation of other metal particles.

This sonochemical reduction method of noble metal ions appears to be promising for the preparation of noble metal colloids in aqueous solution. Further studies of ultrafine particles formed from other transition metals and alloys by ultrasonic irradiation are now underway.

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