Bull. Chem. Soc. Jpn., *61*, *347—350 (1988)*

The Preparation of Colloidal Precious Metal Particles Using Copolymers of Vinyl Alcohol-*N*-Vinylpyrrolidone

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(Received June 18, 1987)

Precious metal particles of platinum and silver have been prepared by the reduction of metal salts dissolved in an aqueous solution of a copolymer of vinyl alcohol and *N*-vinylpyrrolidone with methanol. The stable platinum sols were obtained in the presence of poly(vinyl alcohol), poly(*N*-vinylpyrrolidone), and their copolymers, but their particle sizes hardly changed with the ratio of *N*-vinylpyrrolidone in the copolymer. On the other hand, colloidal stable silver sols were obtained only in the presence of a copolymer. Further, with an increase in the ratio of *N*-vinylpyrrolidone in the copolymer, the particle size of silver became small.

Precious metal particles have been attractive as catalysts[1-3] when it is desirable to use fine monodispersed particles. On the preparation of fine particles, precious metal ions have often been reduced in a mixture of precious metal ions, protective colloids, and a reducing agent. As protective colloids, poly(vinyl alcohol), poly(*N*-vinylpyrrolidone), and poly(methyl vinyl ether)[4-9] have been employed. However, homopolymers are not easily adsorbed on precious metal particles, so monodispersed particles are hard to obtain when they are used.

The objective of this work was to prepare fine monodispersed precious metal particles using copolymers of vinyl alcohol-*N*-vinylpyrrolidone.

Experimental

Materials. The $H_2PtCl_6 \cdot 6H_2O$ was supplied by Tanaka Kikinzoku K.K., while the $AgNO_3$ was obtained from the Tokyo Kasei Co. Ltd. The poly(vinyl alcohol)(PVA) and poly (*N*-vinylpyrrolidone)(PVP) were obtained from Kishida Chemicals Co., Ltd., and the Tokyo Kasei Co., Ltd., respectively. As monomers, vinyl acetate (VAc) and *N*-vinylpyrrolidone(VP) were obtained from Wako Chemical Industries: They were distilled under reduced pressure before use. The other chemicals were of extra pure grades. The water used was purified through the Milli-Q Reagent Water System.

Preparation of Copolymers: Mixtures of VAc and VP in various ratios were added to acetone, and the polymerization was carried out under a nitrogen gas atmosphere at 70 °C, using α,α'-azobisisobutyronitrile as the initiator. Then, the products, as purified with petroleum ether, were dissolved into methanol and saponified upon the addition of sodium methoxide at 40 °C under a nitrogen-gas atmosphere. The samples thus obtained were purified with diethyl ether and acetone.

Measurements: The molecular weights of the samples were determined by means of gel permeation chromatography (Japan Optical Co.) with a column of Shodex OH Pak B800P and B804 (Showa Denkou Co.): Pullulan was used as the standard sample, and a mixture of methanol and water (1 : 1) was used as the solvent.

Determination of the Content Ratio of the Copolymer of Vinyl Alcohol-*N*-Vinylpyrrolidone: Some VAc-VP copolymers were dissolved into acetone, and then sodium hydroxide was added for saponification. After the complete saponification, the remaining sodium hydroxide was back-titrated with hydrochloric acid. From the results of a subsequent titration, the ratio of VA-VP in the copolymers was determined.

Preparation of Colloidal Particles: A polymer (7.5—200 mg) as a protective colloid and a metal salt (0.033 mmol dm^{-3}) were dissolved in a mixed solvent consisting of methanol (25 ml) and water (25 ml). The resulting solution was refluxed to prepare a colloidal dispersion of the metal. In the case of silver nitrate, the concentrations ranged between 0.033 and 0.33 mmol dm^{-3}.

The particle sizes of the precious-metal particles obtained were determined by means of transmission electron microscopy with a Hitachi H 800 microscope.

Results and Discussion

Platinum Sol. Figure 1 shows the relationship between the amount of PVP added and the number-average particle size of platinum. When the amount of PVP was 75 mg, the particle size was smallest in the case of the highest molecular weight of PVP. However, upon the addition of 150—200 mg of PVP, the particle size increased with an increase in the molecular weight of PVP. Similar experiments were also carried out in the case of PVA. It was found that the

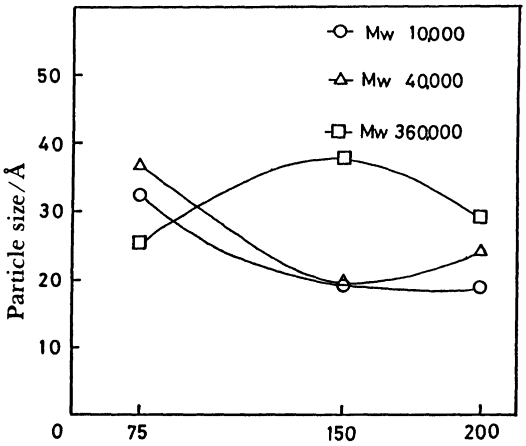

Fig. 1. Mean particle size of platinum sols as a function of molecular weight of PVP.

particle size hardly changed with an increase in the amount of PVA added (M.W.=20000). Further, using PVA (M.W.=88000), stable platinum sols were obtained, but their particle size could not be determined by transmission electron microscopy because extensive coagulation resulted from the evaporation of the solvent from a drop of solution on the support. Accordingly, in order to study the effect of copolymers on the particle size of platinum particles, the molecular weight of the copolymer was controlled to within the range of 30000—60000. The pertinent properties of the copolymers are given in Table 1.

Figure 2 shows the number-average particle size of platinum with the molar ratio of VA or VP in the copolymers. Here, the amount of the copolymers added was 150 mg. From Fig. 2 it can be seen that, except for PVA, the particle sizes of platinum are almost the same for the other copolymers, indicating that the copolymers of VA-VP do not provide a different colloidal protective action from homopolymers (PVA or PVP).

Silver Sol. Keeping constant the amount of copolymers added (150 mg), silver sols were prepared as a function of the amount of silver nitrate. In the case of PVA alone, stable silver sols were not obtained and the

Table 1. Pertinent Properties of Copolymers

Copolymer	Molar ratio in copolymer		Molecular weight
	VA	VP	
A2	0.15	0.85	4.4×10^4
A4	0.35	0.65	6.4×10^4
A8	0.74	0.26	3.1×10^4

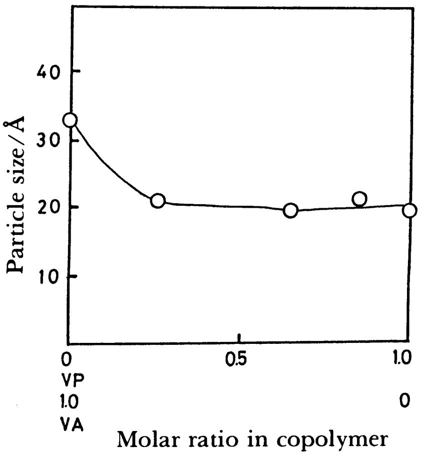

Fig. 2. Mean particle size of platinum sols as a function of molar ratio of VA or VP in copolymers.

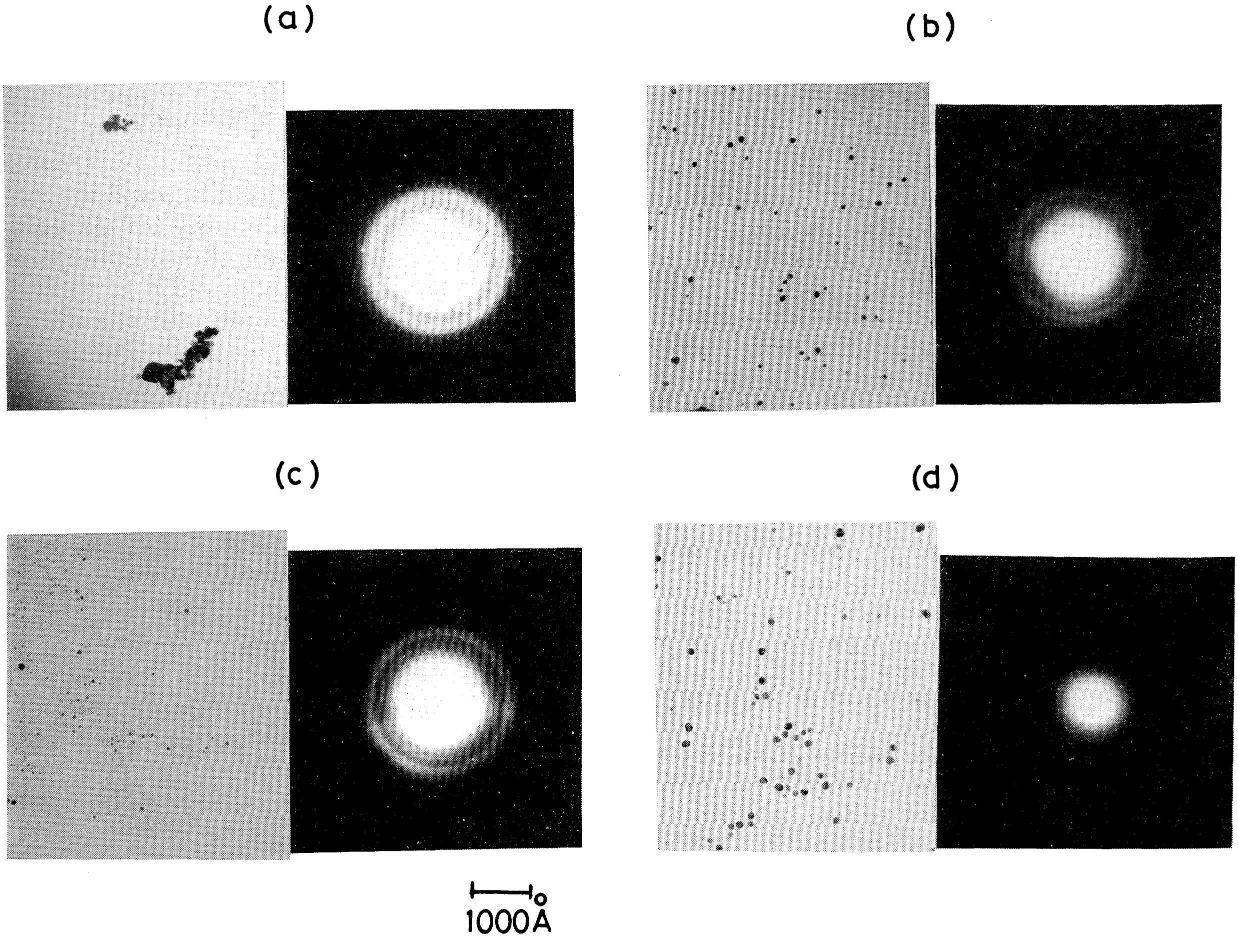

Fig. 3. Electron micrograph and electron diffractogram of colloidal silver sols: (a) PVP, (b) A2, (c) A4, (d) A8.

colloidal dispersions were turbid. This result coincided with that obtained by Hirai et al.[8] Similarly, PVP alone did not provide any stable silver sols. The electron photograph and electron diffractogram of these particles are shown in Fig. 3(a), where their particle sizes range from 300 to 400 Å.

On the other hand, with the copolymers of VA-VP, a transparent silver dispersion was obtained, where the copolymers of A2 and A8 gave yellow sols, and the others, red sols. The electron photograph and electron diffractogram of these stable sols are shown in Fig. 3(b), (c), and (d). The particle size of the silver sols prepared with the copolymers of A2 and A8 was rather monodispersed, being 80—170 Å of diameter, while those of the sols prepared with the copolymer of A4 were both large and small; the former was about 150 Å, and the latter, 50 Å. From the electron diffractogram, the particles can be said to be crystalline, with a diffraction pattern corresponding to the f.c.c. structure of silver.

Thus, the above results confirm that stable silver sols are obtained only by the use of the copolymer of VA-VP.

In order to elucidate the effect of the copolymer on the formation of silver sols, the silver sols were prepared as a function of the amount of copolymer added. In the case of the copolymer A2 (shown in Table 2), yellow silver sols were obtained in the range of 7.5—200 mg. When 15 and 7.5 mg portions were added, the particle sizes were divided into two regions; one was 100—200 Å, and the other, 30—40 Å. In the case of the copolymer A4 (shown in Table 3), the color of sols changed with the amount of the copolymer added; the red sols were obtained in the range of 100—200 mg and 7.5—15.0 mg, and the yellow sols, in the range of 25—75 mg. The electron microscopy shows that, upon the addition of 37.5—75 mg, and 200 mg of the copolymer A4, monodispersed sols are prepared, but the addition of 100—175 mg of the copolymer A4 leads to a broad particle size distribution. Table 4 shows the properties of the silver sols prepared in the presence of the copolymer A8. Upon the addition of less than 37.5 mg of the copolymer A8, no stable sols were obtained, but the addition of 75 mg of the copolymer A8 allowed the preparation of monodispersed sols. Upon the further addition of the copolymer A8, the stable sols were still obtained. Thus, with an increase in the ratio of *N*-vinylpyrrolidone in the copolymers, the particles of silver sols became smaller.

Table 2. Color, Dispersion, and Particle Size of Colloidal Silver with the Copolymer A2

Added amount/mg	Color	Dispersion	Particle size/Å
200	Yellow	Stable	70—120
175	Yellow	Stable	50—200
150	Yellow	Stable	100—160
100	Yellow	Stable	60—150
75	Yellow	Stable	80—150
37.5	Yellow	Stable	70—100
15	Yellow	Stable	100—180, 30—40
7.5	Yellow	Stable	150—200, 30

Table 3. Color, Dispersion, and Particle Size of Colloidal Silver with the Copolymer A4

Added amount/mg	Color	Dispersion	Particle size/Å
200	Red	Stable	60—110
175	Red	Stable	20—180
150	Red	Stable	100—200, 50
100	Red	Stable	100—200
75	Yellow	Stable	60—110
37.5	Yellow	Stable	60—110
25	Yellow	Stable	30—150
15	Red	Stable	20—150
7.5	Red	Stable	100—300, 30—70

Table 4. Color, Dispersion, and Particle Size of Colloidal Silver with the Copolymer A8

Added amount/mg	Color	Dispersion	Particle size/Å
200	Yellow	Stable	50—110, 250
175	Yellow	Stable	50—130
150	Yellow	Stable	80—150
100	Red	Stable	60—170
75	Yellow	Stable	60—110
37.5	Gray	Instable	20—300
25	Gray	Instable	Coagulate
15	Gray	Instable	Coagulate
7.5	Gray	Instable	Coagulate

Consequently, it can be summarized that, upon the addition of the copolymer A2 in the range of 0.5—4 wt%, rather monodispersed silver sols are prepared, while the addition of the copolymer A4 or A8 also leads to the formation of monodispersed silver sols, although the additive concentration is restricted to some degree.

Protective colloids, such as PVA, and PVP, have been used to prepare colloidal precious metal particles because they adsorb on metal particles, resulting in stable sols. In this study, PVA and PVP are found to be effective as a protective colloid for the preparation of colloidal platinum sols. Although Jirgensons et al.[10] have reported that decreasing the degree of the polymerization of PVP results in a depression of the aggregation of precious metal particles, an opposite result is obtained in this study.

In the case of the preparation of silver sols, the copolymers of VA-VP give rather monodispersed silver sols, suggesting that the copolymers of VA-VP are adsorbed effectively on the silver sols. In fact, Ueno[11] has reported that the surface tension of the copolymers of VA-VP decreases with an increase in the VP content and is lower than that of each homopolymer. This result leads to the conclusion that the copolymers of VA-VP can adsorb on a solid surface more easily than homopolymers, resulting in the formation of monodispersed particles as an effective protective colloid.

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