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The Preparation of Organo Colloidal Precious Metal Particles

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Platinum particles were prepared by reducing the hydrogen hexachloroplatinate extracted in organic solvents from an aqueous solution by these extractants:dioctadecyldimethylammonium chloride(DDAC), trioctylmethylammonium chloride(TMAC), and trioctylphosphine oxide(TOPO). The extraction ratio of platinum(IV) increased in chloroform, isobutyl methyl ketone, and cyclohexane with an increase in the concentrations of the extractants, and then approached a constant state. The extracts were reduced by formaldehyde or benzaldehyde in the presence of water and a base (sodium hydroxide or triethylamine) for several hours at 65 °C. The platinum particles obtained in chloroform and isobutyl methyl ketone were very stable; their diameters were 15—25 Å.

The preparation of colloidal metals has long been studied extensively.[1-4] Recently, many investigations of the preparation of particles have concentrated upon precious metals because of their many applications, e.g., as catalysts.[5,6] The greater part of the experiments have been made in an aqueous solution in the presence of surfactants or polymers in order to stabilize the colloidal particles.[5-7] Further, it has been reported[8,9] that the precious metal particles can be prepared in water in oil microemulsions. However, there have been only a few reports on the preparation of precious metal particles in organic solvents, since the solubility of most particle precursors is very low in organic solvents.

On the other hand, metal salts can be transferred into organic solvents by means of solvent extraction.[10-13] This method allows precious metal salt to be extracted in organic solvents as particle precursors of organic precious metal.

The aim of the present work was to prepare platinum metal particles from their salts extracted into organic solvents.

Experimental

Materials. Hexachloroplatinic(IV) acid was supplied by Tanaka Kikinzoku Kogyo K.K. as a hexahydrate ($H_2PtCl_6\cdot 6H_2O$). As extractants, dioctadecyldimethylammonium chloride (DDAC), trioctylmethylammonium chloride (TMAC), and trioctylphosphine oxide (TOPO) were employed. The DDAC was obtained from the Lion Co., Ltd., and was purified once by recrystallization from 2-propanol. The TMAC and TOPO were commercial, extra pure grades from the Tokyo Chemical Industry Co., Ltd., and were used without further purification. The other chemicals were commercial, extra pure grades from Wako Pure Chemical Industries, Ltd. The water used in this experiment was deionized by means of the MILLI-Q Water Purification System.

Procedure. For the extraction, two kinds of solutions were mixed; one was a 10 ml aqueous solution of 0.5 mmol dm^{-3} hexachloroplatinic(IV) acid, while the other was 0—3.0 mmol dm^{-3} of the extractant in chloroform, isobutyl methyl ketone (MIBK), or cyclohexane (in the case of TOPO, 0—2.0 mol dm^{-3} HCl was used). Then, the mixed solution was shaken at 25°C for 12 h to attain an equilibrium of extraction. After the extraction, the concentration of platinum(IV) remaining in the aqueous solution was determined photometrically by means of the tin chloride method. The extraction ratio was calculated from the difference between the initial concentration of Pt(IV) and that remaining in the aqueous phase.

In order to obtain Pt particles, each of the platinum(IV) salts extracted in an organic solvent was directly reduced by several reductants: formaldehyde, benzaldehyde in the presence of sodium hydroxide, triethylamine (TEA) and water, hydrazine, and hydrogen (through bubbling). The subsequent refluxing of the solution under nitrogen gas on a water bath (65 °C) between 15 min and 10 h gave a homogeneous dark brown solution of platinum sols.

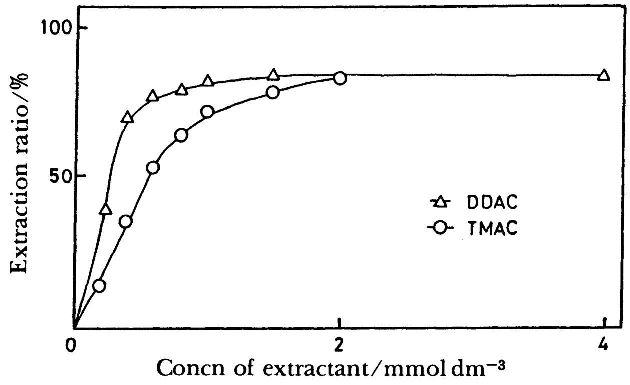

Fig. 1. Effect of concentration of DDAC and TMAC in chloroform on the extraction of platinum(IV).

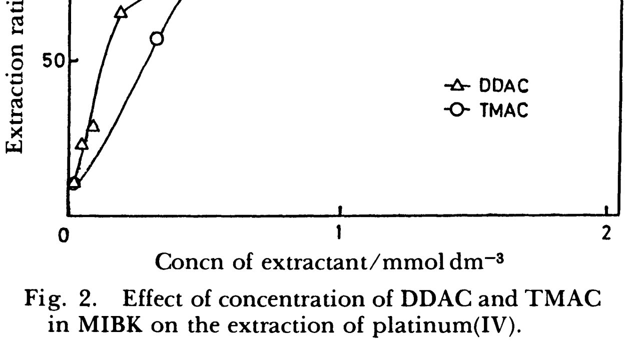

Fig. 2. Effect of concentration of DDAC and TMAC in MIBK on the extraction of platinum(IV).

The Pt-particle sizes were determined by means of transmission electron microscopy with a Hitachi H-800 microscope. The magnification of the electron microscope was 70000—200000. The particle size distribution and the average diameter of the Pt particles were obtained on the basis of these enlarged electron-microscope photographs.

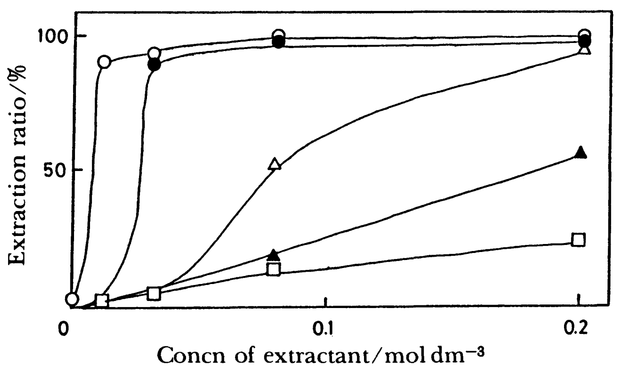

Fig. 3. Effect of concentration of TOPO in cyclohexane on the extraction of platinum(IV): HCl concentration; (□) 0, (▲) 0.1, (△) 0.5, (●) 1.0, (○) 2.0 mol dm^{-3}.

Results and Discussion

The effect of the extractant concentration on the transfer of platinum(IV) salt to an organic solvent was studied. The efficiency of extraction is usually defined as the ratio of the platinum(IV) concentration in an organic solvent against the total platinum(IV) concentration: This is named the "extraction ratio." The extraction ratios of platinum(IV) to chloroform by

Table 1. Properties of Precursors of Platinum Sols by Extraction

Initial concn of Pt	Extractant and concn	Organic solvent	Extraction ratio	Concn of Pt in organic phase
mmol dm^{-3}	mmol dm^{-3}		%	mmol dm^{-3}
0.5	DDAC 1.5	Chloroform	83.6	0.42[D/C]
	TMAC 2.0		82.6	0.42[T/C]
	DDAC 0.5	MIBK	77.0	0.39[D/M]
	TMAC 1.0		98.6	0.49[T/M]
	TOPO 50	Cyclohexane	99.8	0.50[T/H]

Table 2. Properties of Platinum Sols Prepared in Chloroform

Extractant	Reducing agent	Base/H_2O	Reduction	Dispersion
DDAC	Formaldehyde	—	X	—
		NaOH+H_2O	O	Stable
		TEA+H_2O	O	Stable
	Benzaldehyde	—	X	—
		NaOH+H_2O	O	Stable
		TEA	X	—
		TEA+H_2O	O	Stable
	Hydrazine	—	O	Instable
	Hydrogen	—	X	—
TMAC	Formaldehyde	—	X	—
		NaOH+H_2O	O	Stable
		TEA+H_2O	O	Stable
	Benzaldehyde	—	X	—
		NaOH+H_2O	O	Stable
		TEA	X	—
		TEA+H_2O	O	Stable

O: complete reduction, X: incomplete reduction.

Table 3. Properties of Platinum Sols Prepared in MIBK

Extractant	Reducing agent	Base/H_2O	Reduction	Dispersion
DDAC	Formaldehyde	—	X	—
		NaOH+H_2O	O	Instable
		TEA+H_2O	O	Instable
	Benzaldehyde	—	X	—
		NaOH+H_2O	O	Instable
		TEA	X	—
		TEA+H_2O	O	Instable
TMAC	Formaldehyde	—	X	—
		NaOH+H_2O	O	Stable
		TEA+H_2O	O	Stable
	Benzaldehyde	—	X	—
		NaOH+H_2O	O	Stable
		TEA	X	—
		TEA+H_2O	O	Stable

O: complete reduction, X: incomplete reduction.

DDAC and TMAC are plotted against the concentration of the extractant in Fig. 1. It can be seen that the extraction ratios for both extractants increase with an increase in the concentration of the extractant and then approach to a constant state. In the case of DDAC, the extraction ratio reaches above 85% above the concentration of 1.5 mmol dm^{-3}, while the concentration of more than 2 mmol dm^{-3} of TMAC gave a

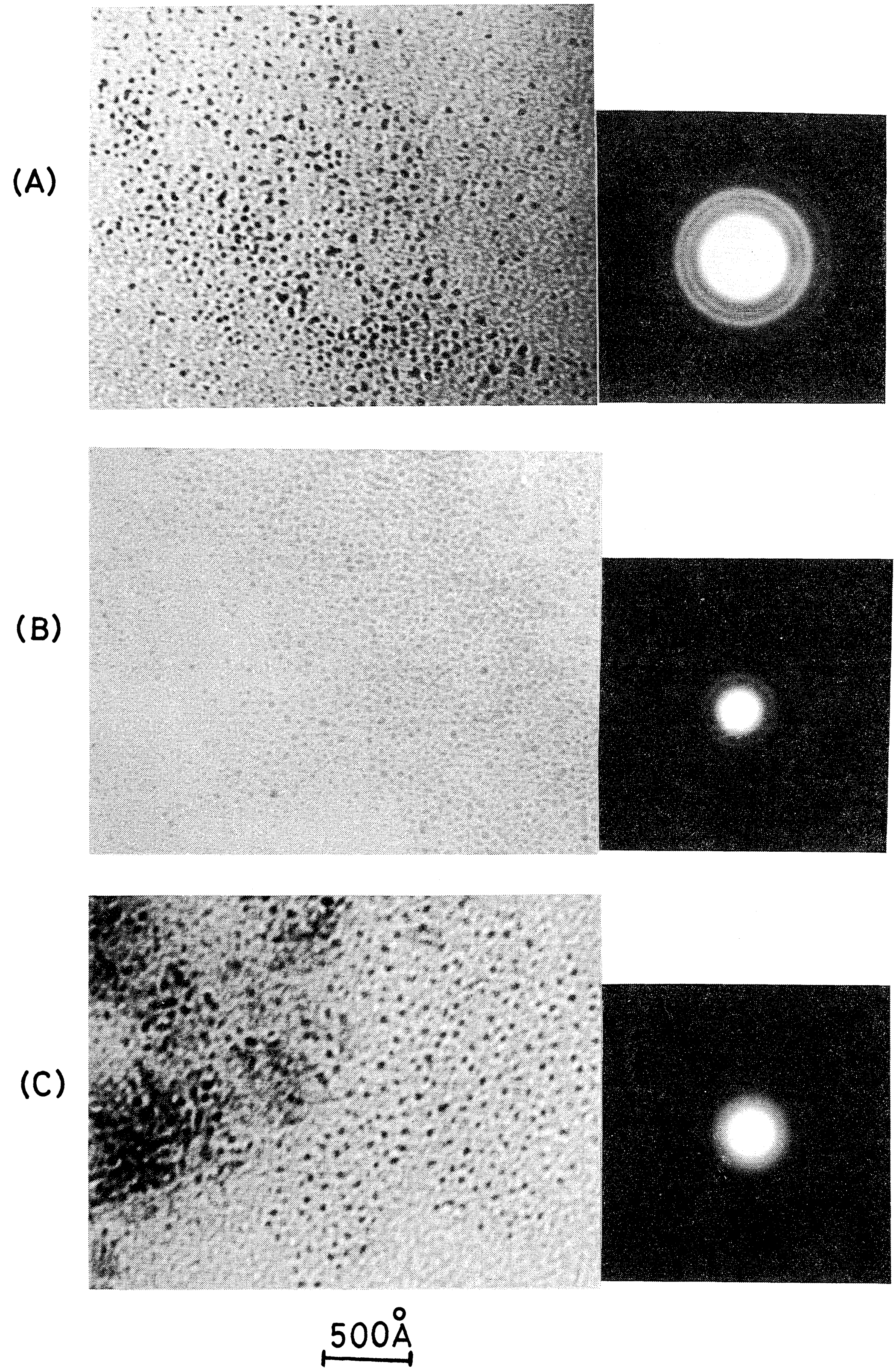

Fig. 4. Electron micrograph and electron diffractogram of platinum sols reduced with formaldehyde from various extracts: (A) D/C, (B) T/M, (C) T/H.

ratio of more than 83%. Similarly, the extraction ratios of platinum(IV) to MIBK by DDAC and TMAC are shown in Fig. 2. When the DDAC and TMAC concentrations were above 1 mmol dm^{-3}, the extraction ratio for the former became more than 80%, while that for the latter was almost 100%. Figure 3 shows the extraction ratio of platinum(IV) in cyclohexane as a function of the concentration of TOPO. It is found that the extraction ratio of platinum(IV) increases with an increase in the concentration of TOPO without any addition of hydrochloric acid, but it is still very low. Upon the addition of hydrochloric acid, however, the extraction ratio increased remarkably: it was almost 100% when the TOPO concentration was 0.05 mol dm^{-3} in the presence of 1.0 mol dm^{-3} hydrochloric acid in water. Thus, it was confirmed that the platinum(IV) salt in an aqueous solution is efficiently transferred to an organic solvent by using adequate extractants.

The particle precursors were prepared under the conditions shown in Table 1. Table 2 shows the conditions of sols preparation from extracts in chloroform and the stability of the sols. The extracts of platinum salt were not reduced by only formaldehyde or benzaldehyde, without any base or water. However, upon the addition of a base and water, very stable Pt sols were obtained. From Table 3 it is apparent that the extracts in MIBK are reduced by formaldehyde or benzaldehyde in the presence of a base and water and that the sols obtained are stable for TMAC, but not for DDAC. In the case of extracts with TOPO in cyclohexane, the sols were also obtained only upon the addition of a base and water, but they were not stable.

The platinum sols particles prepared by the reduction with formaldehyde or benzaldehyde were almost spherical. The extracts obtained by DDAC in chloroform, TMAC in chloroform, DDAC in MIBK, TMAC in MIBK, and TOPO in cyclohexane are abbrevated D/C, T/C, D/M, T/M, and T/H respectively. The electron micrograph and electron diffractogram of particles formed by the reduction of D/C with formaldehyde and sodium hydroxide are shown in Fig. 4(A); their particle-diameter distribution is shown in Fig. 5(A), where the mean particle diameter is 17.5 Å, with a standard deviation of 3.23 Å. Similarly, Figs. 4(B) and 5(B) show the electron micrograph, the electron diffractogram, and the diameter distribution of the platinum particles prepared by the reduction of T/M with formaldehyde and sodium hydroxide; the mean particle diameter was 19.3 Å, with a standard deviation of 3.99 Å. The mean particle diameter of the platinum prepared by the reduction of T/H with formaldehyde and sodium hydroxide was 19.0 Å, and the standard deviation was 4.94 Å, as is shown in Figs. 4(C) and 5(C). The platinum particles prepared by the above method are crystalline, with a diffraction pattern corresponding to the fcc structure of platinum.

The effect of the reaction time on the particle-diameter distribution of the platinum particles produced by the reduction of T/C with benzaldehyde,

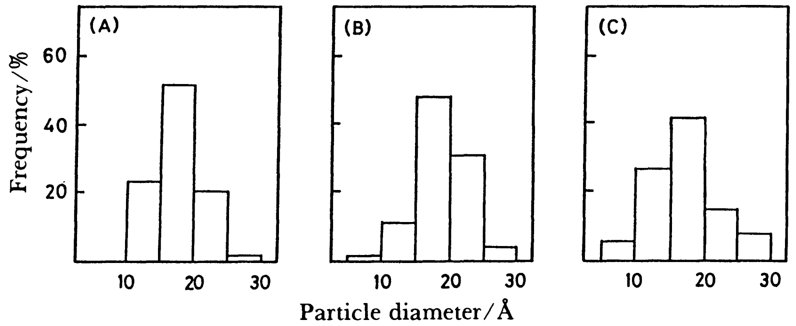

Fig. 5. Particle diameter distribution of platinum sol particle: (A) D/C, (B) T/M, (C) T/H.

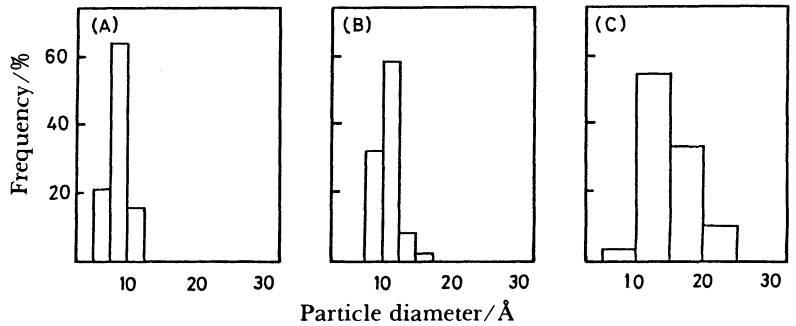

Fig. 6. Particle diameter distribution of platinum sol particles by reduction of T/C with benzaldehyde, triethylamine and water: reaction time; (A) 15, (B) 30, (C) 120 min.

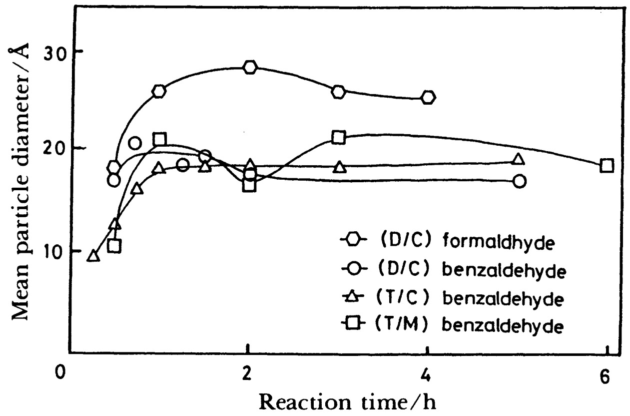

Fig. 7. Relationship between reaction time and mean particle size of platinum sol.

triethylamine, and water was also studied. In Fig. 6 it can be seen that the size of the platinum particles increases with an increase in the reaction time; the mean particle diameters are 8.3, 10.5, and 15.1 Å for 15, 30, and 120 min respectively, while the corresponding deviations are 1.39, 1.62, and 3.07 Å. Further, the plots of the mean particle diameter vs. the reaction time for the four systems are shown in Fig. 7. It is found that the mean particle diameter increases with an increase in the reaction time until about 1 h, and then becomes constant, suggesting that the nucleation of the platinum particle occurs and that the nucleus has grown into a certain constant value during the initial hour. Compared with the reduction of D/C by formaldehyde and benzaldehyde, the former provides larger platinum particles than the latter. This result is, presumably, attributably to the difference between the solubilities of benzaldehyde and formaldehyde in chloroform; benzaldehyde has a higher solubility than formaldehyde.

As a conclusion, it can be said that the preparation of platinum particles in an organic solvent needs water to facilitate the reduction of platinum(IV) with formaldehyde or benzaldehyde. It seems that the reduction of platinum(IV) occurs at the interface between the water and the organic solvent and that the platinum nucleus is produced and grows quickly (in about one hour) at this interface. As a result, platinum particles with diameters in the range of 15—25 Å are obtained. This method can also be used in the preparation of other precious metal particles in organic solvents.

References

1) J. Turkevich, R. C. Stevenson, and J. Hiller, *Discuss. Faraday Soc.*, **11**, 55 (1951).

2) K. Takiyama, *Bull. Chem. Soc. Jpn.*, **31**, 944 (1958).

3) B. V. Enustun and J. Turkevich, *J. Am. Chem. Soc.*, **85**, 3317 (1963).

4) R. M. Wilenzick, D. C. Russell, R. H. Morriss, and S. W. Marshall, *J. Chem. Phys.*, **47**, 533 (1967).

5) H. Hirai, K. Ishihara, and I. Shinohara, *Makromol. Chem. Rapid Commun.*, **2**, 99 (1981).

6) T. Toshima, T. Takahashi and H. Hirai, *Chem. Lett.* **1985**, 1245.

7) J. Kiwi and M. Grätzel, *J. Am. Chem. Soc.*, **101**, 7214 (1979).

8) M. Boutonnet, J. Kizling, and P. Stenius, *Colloids and Surfaces*, **5**, 209 (1982).

9) K. Kurihara, J. Kizling, P. Stenius, and J. H. Fendler, *J. Am. Chem. Soc.*, **105**, 2574 (1983).

10) M. A. Khattak and R. J. Magee, *Talanta*, **12**, 733 (1965).

11) M. J. Cleare, P. Charlesworth, and D. J. Bryson, *J. Tech. Biotechnol.*, **29**, 210 (1979).

12) M. Majski, *J. Radioanal. Chem.*, **46**, 239 (1978).

13) T. Sekine and Y. Hasegawa, *Bunseki*, 1978, 627.

14) I. Maziekien, L. Ermanis and T. J. Walsh, *Anal. Chem.*, **32**, 645 (1960).