CHEMISTRY LETTERS, pp. 1245-1248, 1985.

COLLOIDAL PLATINUM CATALYSTS PREPARED BY HYDROGEN- AND PHOTO-REDUCTION IN THE PRESENCE OF SURFACTANT

Naoki TOSHIMA,* Tadahito TAKAHASHI, and Hidefumi HIRAI

Department of Industrial Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

Chloroplatinic acid in an aqueous solution was reduced by hydrogen molecules or photo-irradiation in the presence of surfactants to produce colloidal dispersions of platinum protected by the surfactants. The particles of the colloidal platinum prepared by photo-reduction were smaller in size and more narrowly dispersed than those prepared by hydrogen-reduction. They worked as highly active catalysts for hydrogenation of olefins.

Noble metals are often used for the catalysts for various organic reactions, and are known to be extremely active in the colloidal state. We have reported that the colloidal dispersions of noble metals are prepared by refluxing the alcoholic solution of the noble metal ions in the presence of some water-soluble vinyl polymers like poly(N-vinyl-2-pyrrolidone).[1] These colloidal metals act as active and selective catalysts in the hydrogenation of olefins[2] and dienes.[3] In an aqueous solution, the backbone of the water-soluble vinyl polymer forms a hydrophobic domain, which surrounds colloidal particles, whereas the hydrophilic pendant groups of the polymer interact with water. Thus, the polymer disperses the particles in water. In the present letter, surfactants were used instead of water-soluble vinyl polymers to protect the colloidal particles. In other words, the colloidal dispersions of platinum were prepared by reducing chloroplatinic acid in the presence of various types of surfactants. For reduction of Pt(IV) ion in this system, photo-irradiation was found to be the most appropriate method. Here, we would like to report the preparation of colloidal platinum by hydrogen- and photo-reduction in the presence of surfactants and its application for a hydrogenation catalyst of olefins.

Dodecyltrimethylammonium chloride (DTAC) and sodium dodecylsulfate (SDS) were used as cationic and anionic surfactant, respectively. The alcohol reduction method[1] was not suitable for preparation of colloids in the present system since the micelles made by surfactants are easily destroyed by the coexistence of alcohol or treatment with heat. So, contact with hydrogen gas (hydrogen-reduction)[4] and photoirradiation (photo-reduction)[5] were chosen as reduction methods which would not destroy the micelles.

In hydrogen-reduction, an aqueous solutions (10 cm^3) of 0.2 mmol dm^{-3} chloroplatinic acid and a chosen concentration of a surfactant were deaerated and put into contact with atmospheric hydrogen at room temperature by stirring the

Table 1. Hydrogen- and photo-reduction of chloroplatinic acid in the presence of surfactants[a)]

Reducing agent	Surfactant		State of reduced Pt[d)]
	Abbreviation[b)]	Concentration / mmol dm^{-3}	
H_2	SDS	100	ppt
	SDS	20	ppt
	SDS	7[c)]	colloid
	SDS	3	ppt
	DTAC	140	ppt
	DTAC	100	colloid
	DTAC	20[c)]	colloid
	DTAC	10	ppt
	None	0	ppt
Light	SDS	100	colloid
	SDS	8[c)]	colloid
	SDS	2	colloid-ppt[e)]
	DTAC	100	colloid
	DTAC	20[c)]	colloid
	DTAC	10	ppt
	None	0	ppt

a) $[H_2PtCl_6] = 0.2$ mmol dm^{-3}. b) SDS; sodium dodecylsulfate, DTAC; dodecyltrimethylammonium chloride. c) Near the critical micelle concentration of each surfactant. d) ppt; precipitate e) Precipitation after several days' standing.

solution. The solution turned brownish in less than 20 min. The results are shown in Table 1. Homogeneous colloidal dispersions of platinum were obtained near the critical micelle concentration (CMC) of the surfactant used and they are quite stable for more than several months. Above or below CMC, the reduced platinum formed precipitates. Colloidal dispersions were obtained only in the narrow range of the concentration of the surfactant. Moreover, there was a trouble in reproducibility in the preparation of homogeneous dispersions.

On the contrary, photo-reduction was found to be a very good method. The same solutions of chloroplatinic acid and a surfactant as in hydrogen-reduction were deaerated and irradiated with 500 W super-high-pressure mercury lamp through a Pyrex filter at room temperature for 2 - 15 h until the solution turned brownish. As shown in Table 1, the effect of surfactant concentration was much different from that observed in the case of hydrogen-reduction. The colloidal dispersions of platinum were obtained even at concentration of the surfactant higher than the CMC. They are also quite stable. In some cases, the colloidal dispersion was obtained even below the CMC, but this colloidal dispersion was not so stalbe that it precipitated after several days' standing. This phenomenon may be attributed to the temporary decrease of CMC of the system by the formation of colloidal platinum.

Figure 1 shows electron micrographs of colloidal platinum particles prepared

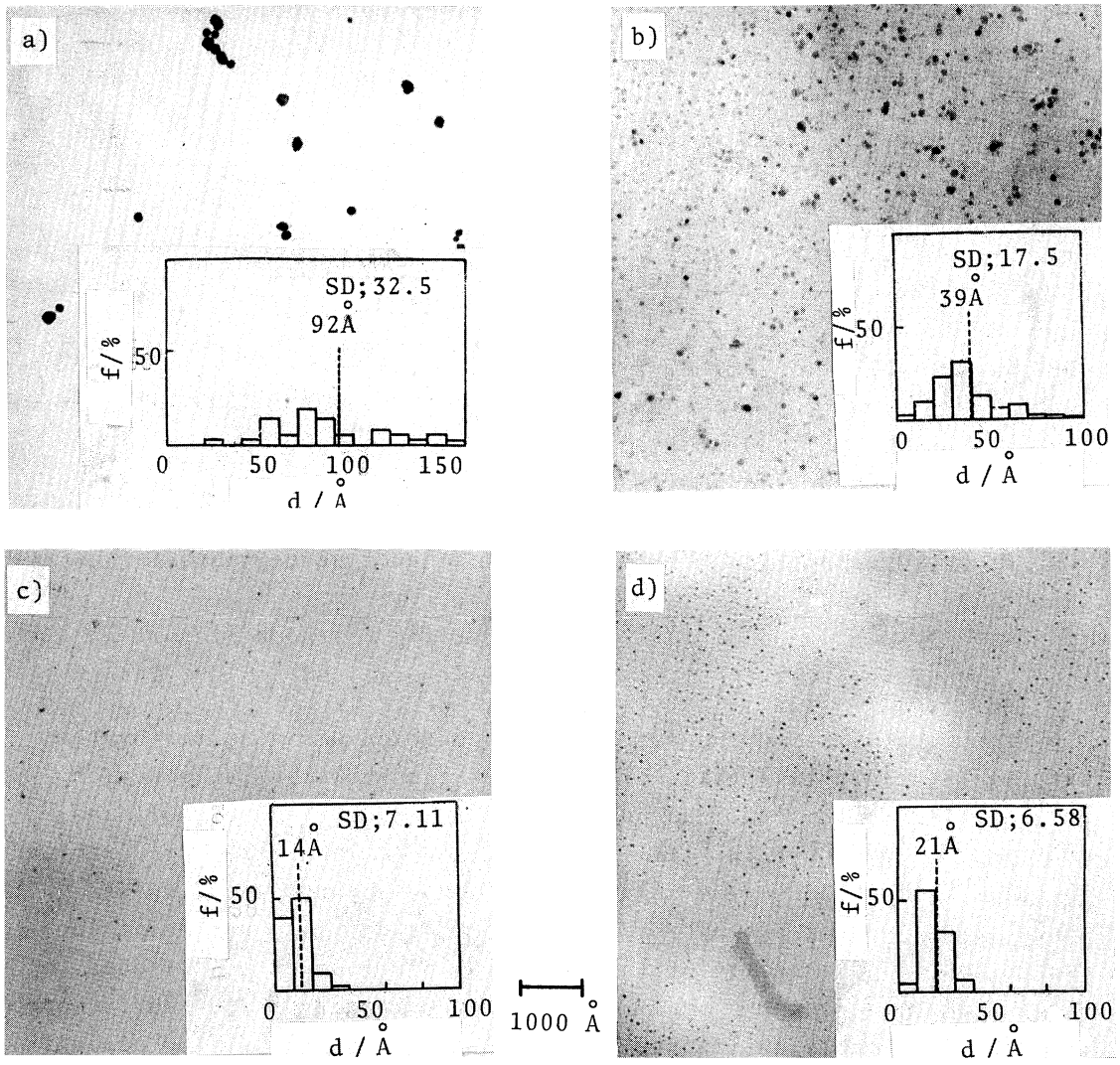

Fig. 1. Electron micrographs and size distributions of colloidal platinum particles prepared by hydrogen-reduction in the presence of a) SDS, b) DTAC, and photo-reduction in the presence of c) SDS, d) DTAC. See text for details.

by hydrogen-reduction and photo-reduction methods. The hydrogen-reduction method gives very big particles, which are widely distributed in size. On the other hand, the particles obtained with photo-reduction are small and nearly monodispersed.

The particle size distributions (frequency f vs. diameter d) obtained from the electron micrographs, as well as the average particle diameters (dotted lines) and the standard deviations (SD), are also shown in the Fig. 1. These data clearly point out that photo-reduction is a better method than hydrogen-reduction in order to obtain fine colloidal platinum protected by surfactants.

The catalytic activity of colloidal platinum thus obtained was examined in the hydrogenation of vinyl acetate (VAc), which was carried out under atmospheric hydrogen at 30 °C adding 1.08 mmol VAc into 10 cm^3 solution of 0.2 mmol dm^{-3}

Table 2. Hydrogenation of vinyl acetate with various colloidal platinum catalysts[a)]

Pt catalyst		Aggregation time[f)]	Hydrogen uptake
Abbreviation	Average diameter / Å	min	$cm^3\ min^{-1}\ Pt\text{-}mol^{-1}$
Pt-DTAC-hν[b)]	21	>1500	78
Pt-PVP-EtOH[c)]	26	40	43
Pt-DTAC-H_2[d)]	39	130	10.4
Pt black[e)]	~500	0	0.67

a) [Pt] = 0.2 mmol dm^{-3}, at 30 °C, p_{H_2} = 1 atm. [Vinyl acetate] = 108 mmol dm^{-3}.
b) Colloidal Pt prepared by photo-reduction in the presence of dodecyltrimethylammonium chloride (DTAC) (20 mmol dm^{-3}).
c) Colloidal Pt prepared by methanol-reduction in the presence of poly(N-vinyl-2-pyrrolidone) (20 mmol dm^{-3}).
d) Colloidal Pt prepared by hydrogen-reduction in the presence of DTAC (20 mmol dm^{-3}).
e) Commercial. f) Reaction time for visual observing of the aggregates.

colloidal platinum catalysts. The rate of hydrogenation was measured by the initial rate of the hydrogen uptake. The results are shown in Table 2 along with the average diameter of the platinum particles. The photo-reduced colloidal platinum catalyst is the best in activity among the platinum catalysts examined. This colloidal catalyst was very stable as well, thus no precipitation was observed even at the end of the hydrogenation and the activity was maintained when it was reused. The activity of the colloidal platinum catalyst seems to depend on the particle size, the smaller, the better. That is, the surface area of the catalyst is probably an important factor to increase catalytic activity.

The present work was partially supported by the Iwatani Naoji Foundation and the Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture.

References

1) H. Hirai, Y. Nakao, and N. Toshima, J. Macromol. Sci.-Chem., A12, 1117 (1978); A13, 727 (1979).
2) H. Hirai, Y. Nakao, N. Toshima, and K. Adachi, Chem. Lett., 1976, 905; H. Hirai, Y. Nakao, and N. Toshima, ibid., 1978, 545.
3) H. Hirai, H. Chawanya, and N. Toshima, Makromol. Chem., Rapid Commun., 2, 909 (1981); Bull. Chem. Soc. Jpn., 58, 682 (1985).
4) A. Skita and W. A. Meyer, Ber. Dtsch. Chem. Ges., 45, 3579 (1912); L. D. Rampino and F. F. Nord, J. Am. Chem. Soc., 63, 2745 (1941).
5) B. Kraeutler and A. J. Bard, J. Am. Chem. Soc., 100, 4317 (1978); K. Kurihara, J. Kizling, P. Stenius, and J. H. Fendler, ibid., 105, 2574 (1983).

(Received June 11, 1985)