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Colloidal Dispersions of Platinum and Palladium Clusters Embedded in the Micelles. Preparation and Application to the Catalysis for Hydrogenation of Olefins

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Colloidal dispersions of platinum and palladium clusters were prepared by the reduction of the corresponding metal salts in the presence of various surfactants. Hydrogen- and photo-reduction methods were examined for the micellar solution of hexachloroplatinic acid. The photo-reduction was proved to be more suitable than the hydrogen-reduction from the viewpoint of small size and good dispersion in the colloidal clusters. The higher surfactant concentration than the critical micelle concentration (cmc) is favorable for the production of the homogeneous colloidal dispersions. The photo-reduction method is also available for the case of palladium. The colloidal platinum and palladium clusters, thus obtained, act as highly active catalysts for the hydrogenation of olefin in an aqueous solution. The colloidal clusters prepared by the photo-reduction method showed higher activity than those prepared by other methods. The roles of the surfactant micelle for the hydrogenation are not only protecting hydrophobic colloidal particles, but also both solubilizing the hydrophobic substrates in an aqueous solution and assisting their approach toward the active site on the surface of the cluster particles. In the hydrogenation of unsaturated fatty acids, the surfactant micelle surrounding the clusters can control the orientation of the substrates, resulting in novel regioselective hydrogenation.

Ultrafine metal particles or metal clusters are of wide interest not only because of their large surface area, but also because of their specific functions which are different from those of either bulk metal solids or metal atoms.1) There have recently been a number of researches studying the preparation and functions of metal clusters. Their applications to physical, chemical and biological fields are now proceeding, such as photoenergy conversion with semiconductors,2) catalyses for various organic reactions,3) and medical applications.4)

Their application to catalysis is one of the most widely investigated fields. Since noble metals are often used as catalysts for various organic reactions, their ultrafine particles are expected to produce specific catalytic functions which are different from those of the bulk metal solids and the metal atoms, for example, the selectivity as well as the efficiency originated from the increase in the surface area.

The present authors have reported on the preparation of the colloidal dispersions of noble metal clusters by refluxing the solution of metal salts in alcohol in the presence of such water-soluble polymers as poly(*N*-vinyl-2-pyrrolidone) (PVP).5) In this reaction, the water-soluble polymer and the alcohol act as a protective colloid and a reducing agent, respectively. The colloidal dispersions, thus obtained, involve metal clusters with nearly uniform size (e.g., 0.9, 2.4, and 3.4 nm in the average diameters). Those noble metal clusters act as highly active, selective catalysts for the hydrogenation of olefins or dienes.6) The polymer protecting the colloidal clusters is also expected to introduce new functions to the clusters as catalysts. In general, water-soluble polymers are expected to interact strongly with the surface of colloidal metal particles at the hydrophobic main chains or branched groups. This interaction could produce a new reaction field which would result specific activity and/or selectivity.

In the present study, the surfactants were chosen as protective colloids for colloidal dispersions of the platinum or palladium clusters, instead of the water-soluble polymers.7) The surfactants are known to have the function to solubilize hydrophobic substances in an aqueous solution. The method to prepare colloidal dispersions of noble metal clusters in the presence of surfactants has scarcely been developed. Although some of the surfactant-protected colloids have actually been reported, they have been prepared by the addition of surfactants soon after a reduction of the metal ions by sodium citrate without any specific protective colloids.8)

The present paper reports on the methods examined to prepare colloidal dispersions of noble metal clusters in the presence of surfactants, as well as their application to a catalyst for hydrogenations. The effects of the hydrophobic field produced by the surfactant micelles upon the catalysis for the hydrogenation of various olefins are discussed.

Experimental

Materials. The structures of the surfactants used as protective colloids in this study are illustrated in Fig. 1. Sodium dodecyl sulfate (SDS) and dodecyltrimethylammonium chlo-

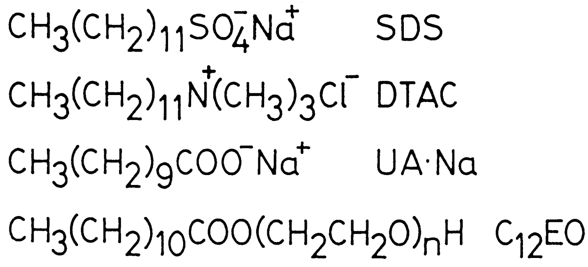

Fig. 1. Structures of the surfactants used for the preparation of colloidal platinum dispersions.

ride (DTAC) were purchased from Tokyo Kasei Co., Ltd. and purified by recrystallization from ethanol and ethanol–diethyl ether, respectively. Nonionic surfactant polyethylene glycol monolaurate ($C_{12}EO$) and water-soluble polymers, poly(*N*-vinyl-2-pyrrolidone) (PVP, Tokyo Kasei Co., Ltd. PVP-K30, M.W.=40000), polyethylene glycol (PEG, Yoneyama Yakuhin Kogyo Co., Ltd. PEG 4000), and propylene oxide–ethylene oxide block copolymer (PO–EO, Sanyo Kasei Co., Ltd.) were commercially purchased and used without further purification. Vinyl acetate and 10-undecenoic acid were purified by distillation; other olefins, such as 2-undecenoic acid and oleic acid, were used as received.

Preparation of Colloidal Dispersions of Noble Metal Clusters. 1) Hydrogen Reduction Method: An aqueous solution of 0.2 mmol dm^{-3} hexachloroplatinic acid (H_2PtCl_6) containing various concentrations of a surfactant was degassed by freeze-thaw cycles and displaced by hydrogen gas. The solution was stirred at room temperature under a hydrogen atmosphere until the color of the solution turned brownish.

2) Photoreduction Method: Photoreduction was performed by visible-light irradiation (by a Pyrex filter) of the same degassed solution at room temperature for 2 h with a 500 W superhigh pressure mercury lamp (Ushio). In the case of photo-reduction of palladium chloride, $PdCl_2$ could be dissolved in water by adding an equimolar amount of hydrochloric acid. The photo-reduction conditions of the palladium ion are the same as that for the platinum system.

Transmission Electron Micrograph of the Colloidal Dispersions of Noble Metal Clusters. The formation of noble metal clusters was confirmed using a transmission electron microscope (TEM, Hitachi HU-12A, x100000). The carbon-supported Cu mesh was used as the support for the sample. The particle-size distributions were determined using an enlarged photograph of the TEM.

Hydrogenation of Olefins. Ten cm^3 of the colloidal platinum or palladium dispersions (0.2 mmol dm^{-3}) were kept under 1 atm hydrogen atmosphere at 30 °C until no further hydrogen gas was absorbed. A designed amount of the olefin was then added to the solution, and the rate of hydrogen uptake under the same conditions was measured using a gas burette. The catalytic activities were compared with the initial rate of hydrogen uptake.

Results

Preparation of Colloidal Dispersion in the Presence of Surfactants. In the present investigation, an alcohol-reduction, a hydrogen-reduction, and a photo-reduction method were compared in order to prepare the colloidal dispersions of platinum and palladium clusters in the presence of surfactants. The alcohol-reduction was examined using the same procedure and under the same conditions as those described in the previous reports using surfactants instead of linear polymers, since this is a characteristic method used to prepare stable colloidal dispersions of fine noble-metal clusters protected by polymers.[9] It was then found that this is not a suitable method for the present surfactant system. Refluxing a solution mixed with alcohol resulted in the deposition of the metal precipitate in all cases examined. The coexistence of an organic solvent, such as alcohol, and treatment by heat are undesirable conditions for the present system, since they might cause destruction of the micelles. Thus, other methods are required to prepare colloidal dispersions when the surfactant is used as the protective colloid instead of polymers. Concerning the undesirable conditions for the the existence of surfactants, we chose hydrogen- and photo-reductions as favorable methods for a system involving surfactants, since these methods can be performed at room temperature in pure water without any organic solvent.

A hydrogen-reduction method is commonly used for the preparation of colloidal dispersions of noble-metal catalysts in the presence of polymers.[10] Table 1 shows the resulting state of platinum produced by the reduction of platinum ions with hydrogen gas under various concentrations of the anionic and the cationic surfactants. In the hydrogen-reduction method, colloidal dispersions of platinum were obtained within a limited range of the surfactant concentration: around the critical micelle concentration (cmc) of each surfactant. Moreover, the method has problems regarding its reproducibility for the formation of stable dispersions of

Table 1. Hydrogen-Reduction of Hexachloroplatinic Acid in Water in the Presence of Various Surfactants[a]

Surfactant		State of reduced platinum
Name[b]	Concentration/mmol dm^{-3}	
SDS	100	Ppt.
SDS	20	Ppt.
SDS	7 (cmc)	Dispersion
SDS	3	Dispersion
DTAC	140	Ppt.
DTAC	100	Dispersion
DTAC	20 (cmc)	Dispersion
DTAC	10	Ppt.
None	0	Ppt.

a) [H_2PtCl_6]=0.2 mmol dm^{-3}. *P*(H_2)=1 atm. b) See Fig. 1 for abbreviation.

Table 2. Photo-Reduction of Hexachloroplatinic Acid in Water in the Presence of Various Surfactants[a]

Surfactant		State of reduced platinum
Name[b]	Concentration/mmol dm^{-3}	
SDS	100	Dispersion
SDS	8 (cmc)	Dispersion
SDS	2	Dispersion[c]
UA Na	100	Dispersion
UA Na	50 (cmc)	Dispersion
UA Na	10	Ppt.
DTAC	100	Dispersion
DTAC	20 (cmc)	Dispersion
DTAC	10	Ppt.
$C_{12}EO$	100	Dispersion
$C_{12}EO$	50	Dispersion
None	0	Ppt.

a) [H_2PtCl_6]=0.2 mmol dm^{-3}. b) See Fig. 1 for abbreviation. c) Precipitated in the long period of time.

noble-metal particles.

In the case of the photo-reduction, however, the situations were quite different. Table 2 shows the results regarding the photo-reduction of hexachloroplatinic acid. The surfactant concentration dependence which was seen in the hydrogen-reduction was not observed in this case (vide infra for the discussion on this difference). The colloidal dispersions of platinum were easily produced when the surfactant concentration was higher than cmc, and sometimes even in the case of a little lower concentration than cmc. The colloidal dispersions of platinum, thus obtained, are stable, even when they are kept at room temperature under air.

In the case of palladium chloride, the same photo-reduction method is available for preparing a colloidal dispersion. However, it took much longer time to form zero-valent palladium clusters than in the case of hexachloroplatinic acid. It took about 24 h for palladium ions to be completely reduced to the palladium clusters, although (at most) 1 h in the case of platinum. The palladium clusters, thus obtained, can be gradually oxidized under the open air at room temperature as shown in Fig. 2. Thus, aqueous dispersion of the colloidal palladium clusters kept under air for three months have the adsorption peak at ca. 420 nm due to palladium chloride.[11]

The photo-reduction method is also available for the production of metal clusters in the presence of water-soluble polymers. The results are summarized in Table 3. Colloidal dispersions, however, are obtained only in the case of surface active polymers comprising the hydrophobic main chain and the hydrophilic side chains, like PVP. In the presence of PEG or the PO–EO copolymer, which has no hydrophobic main chains, no homogeneous colloidal dispersions were obtained.

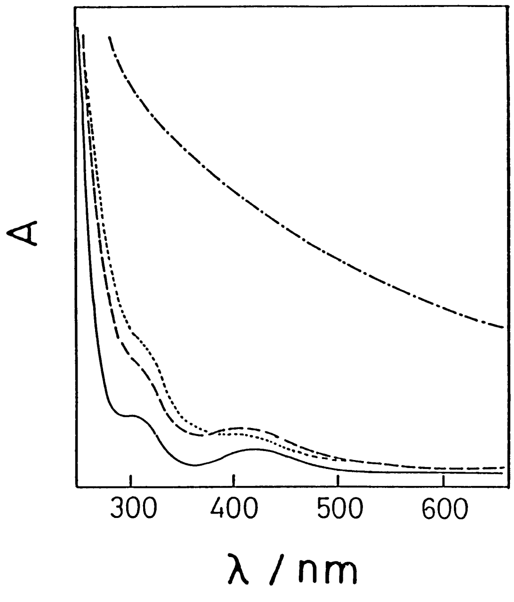

Fig. 2. Absorption spectra of the aqueous dispersion of collidal palladium clusters protected by $C_{12}EO$ as prepared (—·—), that kept under air for 3 months after the preparation (------), and an aqueous solution of the palladium ions in the presence (— —), and the absence (——) of $C_{12}EO$. [Pd]=0.2 mmol dm^{-3}.

Transmission electron micrographs of the colloidal platinum particles prepared by the hydrogen- and the photo-reduction are collected in Fig. 3. These micrographs clearly indicate that the colloidal particles obtained by hydrogen-reduction are relatively large in size and wide in size distribution compared with those obtained by photo-reduction in the present investigation and by alcohol-reduction in a previous report.[5] The visible-light irradiation produces particles with a narrow size distribution, which ranges from 1 to 2 nm in diameter. Figure 4 illustrates the histograms, indicating the particle size distributions of the colloidal platinum particles. These histograms are characteristic of each reduction method. The values of the standard deviations of the particle-size distributions shown in the Fig. 4 clearly indicate the width of the size distributions of the colloidal dispersions. The standard deviations of the photo-reduced particles are entirely less than those of the hydrogen-reduced ones.

Catalytic Activity of Colloidal Dispersion of Platinum Cluster for Hydrogenation of Olefins. Noble metals are often used as active catalysts for the hydrogenation of olefins. The surfactant micelle-protected colloidal platinum prepared in the present study was at first applied to catalysis for the hydrogenation of vinyl acetate. In Table 4 the catalytic activities are estimated by the initial rates of hydrogen uptake along with the

Table 3. Photo-Reduction of Hexachloroplatinic Acid in the Presence of Various Water-Soluble Polymers[a)]

Polymer	State of reduced platinum
Poly(*N*-vinyl-2-pyrrolidone)	Dispersion
Poly(sodium acrylate)	Dispersion
Polyethylene glycol	Ppt.
PO–EO block copolymer[b)]	Ppt.

a) $[H_2PtCl_6]$=0.2 mmol dm^{-3}, [Polymer]=100 mmol dm^{-3} in water. b) Propylene oxide–ethylene oxide block copolymer.

Table 4. Rate of Hydrogen Uptake in Hydrogenation of Vinyl Acetate with Colloidal Platinum Cluster Catalysts[a)]

Pt cluster[b)]	Initial rate	Average diameter
	cm^3 min^{-1} Pt-mmol^{-1}	nm
Pt-DTAC (P)	78	2.1
Pt-$C_{12}EO$ (P)	263	2.5
Pt-PVP (P)	40	1.4
Pt-DTAC (H)	10	3.9
Pt-PVP (A)	43	2.6
Pt black	0.67	>50

a) [Pt]=0.2 mmol dm^{-3}, at 30 °C, $P(H_2)$=1 atm. b) See text for abbreviation. P: Photo-reduction method, H: Hydrogen-reduction method, A: Alcohol reduction method.

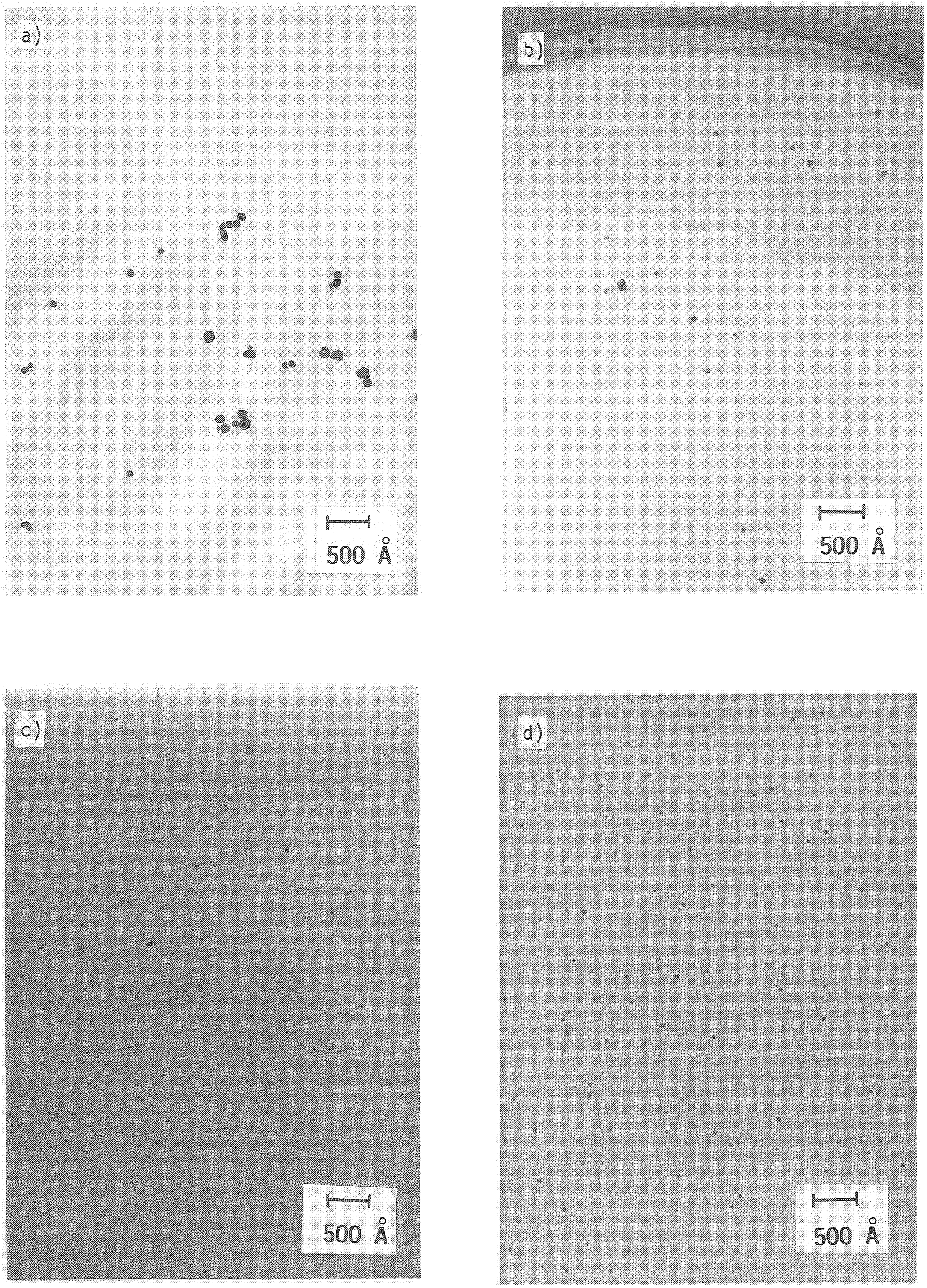

Fig. 3. Electron micrographs of colloidal platinum particles prepared in the presence of surfactant micelles. a) Pt–SDS/hydrogen-reduction, b) Pt–DTAC/hydrogen-reduction, c) Pt–SDS/photo-reduction, d) Pt–DTAC/photo-reduction.

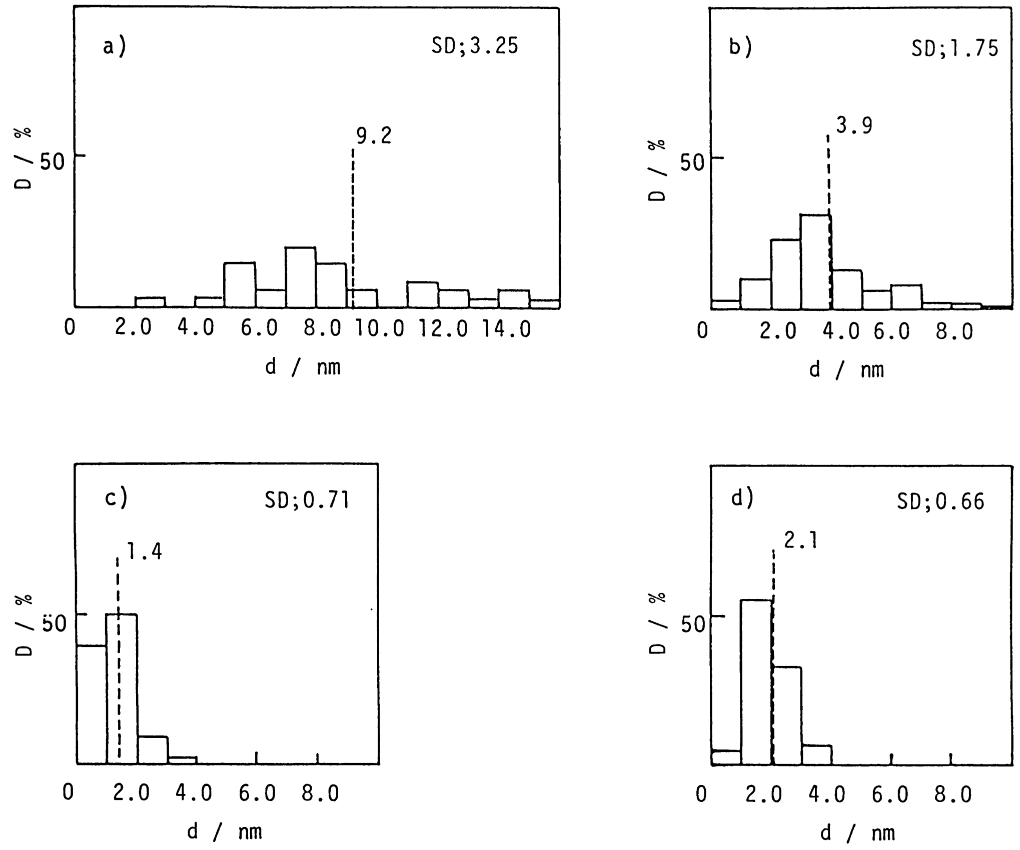

Fig. 4. Particle size distributions of colloidal platinum particles protected by surfactant micelles. a) Pt–SDS/hydrogen-reduction, b) Pt–DTAC/hydrogen-reduction, c) Pt–SDS/photo-reduction, d) Pt–DTAC/photo-reduction. Broken lines indicate the average diameters. SD means standard deviation.

average diameters of the cluster particles. The colloidal dispersions of platinum clusters revealed much higher activity than the commercially available platinum black catalyst. The platinum clusters prepared by photo-reduction are the most active among those examined in the present investigations.

The dependence of the hydrogenation rate upon the kind of substrate was examined for a nonionic surfactant-protected platinum cluster catalyst, which was proved to be the most active platinum catalyst shown in Table 4. Figure 5 illustrates the hydrogen uptake profiles in the hydrogenation of unsaturated fatty acids catalyzed by nonionic surfactant-protected platinum clusters. The catalytic activity varies with the substrates; that is, the hydrogenation rate depends on the location of a double bond in the alkyl chain of the unsaturated fatty acid. Higher activity was obtained for the hydrogenation of 10-undecenoic acid, whose double bond is located at the end of a hydrophobic methylene chain, than for that of the other substrates having their double bonds at the center of the methylene chain, or next to the hydrophilic carboxylic group. The same results as the case of platinum were also obtained in the case of surfactant-protected palladium clusters, as is shown in Fig. 6.

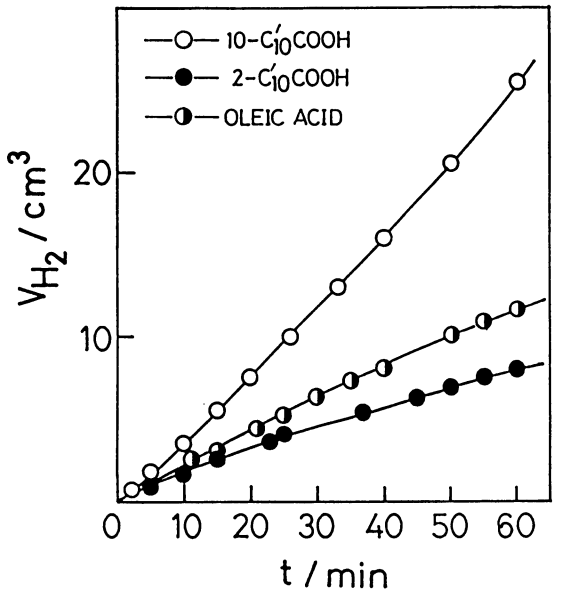

Fig. 5. Time dependence of hydrogen uptake (V_{H_2}) in the hydrogenation of unsaturated fatty acids by the nonionic surfactant-protected platinum cluster catalyst. (○): 10-undecenoic acid, (◑): oleic acid, (●): 2-undecenoic acid. [Pt]=0.2 mmol dm^{-3}, [C$_{12}$EO]=100 mmol dm^{-3}, [substrate]=0.01 mmol dm^{-3}, 30 °C, P(H$_2$)=1 atm.

Table 5. Initial Rates of Hydrogen Uptake in the Hydrogenation of Unsaturated Fatty Acids and Their Sodium Salts Catalyzed by Various Types of Colloidal Noble Metals[a]

Catalyst	Initial rate/$cm^3\,min^{-1}$ Metal-$mmol^{-1}$ [b]		Selectivity
	10-$C'_{10}COOH$	2-$C'_{10}COOH$	R_{10}/R_2 [c]
Pt-$C_{12}EO$	250	90	2.78
Pt-PVP	188	156	1.20
Pd-$C_{12}EO$	730	144	5.08
Pd-$C_{12}EO$	580*	94*	6.23
Pd-PVP	320	240	1.33
Pd-PVP	376*	69*	5.45

a) [Metal]=0.2 mmol dm^{-3}, [Substrate]=0.01 mmol dm^{-3} at 30 °C, $P(H_2)=1$ atm. b) 10-$C'_{10}COOH$: 10-undecenoic acid, 2-$C'_{10}COOH$: 2-undecenoic acid. The initial rate with asterisk were obtained by using the corresponding sodium salts as substrates. c) The ratio of initial rates of hydrogenation of each substrate.

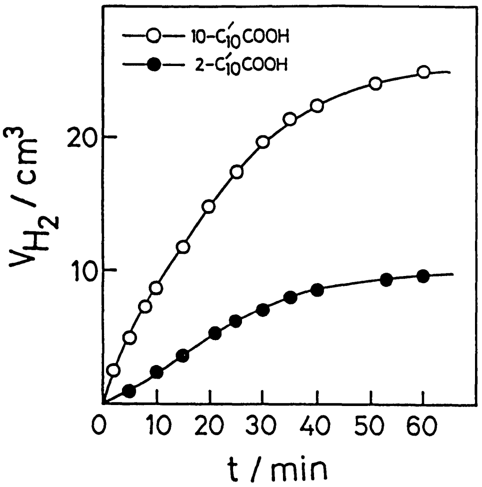

Fig. 6. Time dependence of hydrogen uptake in the hydrogenation of unsaturated fatty acids by the nonionic surfactant-protected palladium cluster catalyst. (○): 10-undecenoic acid, (●): 2-undecenoic acid. The conditions are the same as Fig. 5.

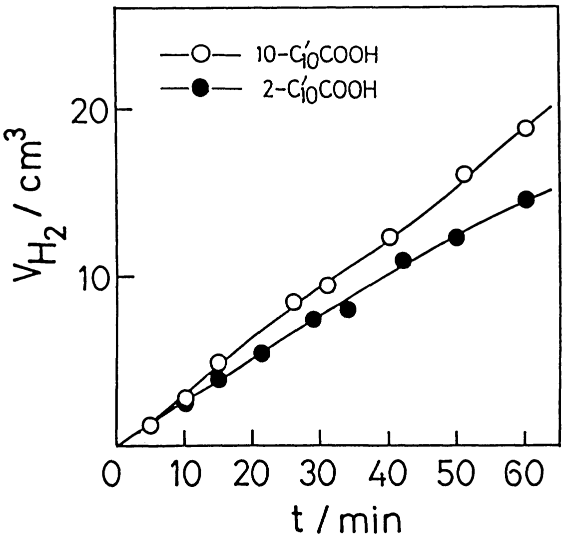

Fig. 7. Time dependence of hydrogen uptake in the hydrogenation of unsaturated fatty acids by polymer-protected platinum cluster catalyst. (○): 10-undecenoic acid, (●): 2-undecenoic acid. The conditions are the same as Fig. 5.

These regioselectivities were characteristic of surfactant-protected clusters. In fact, in the case of the commercial palladium black catalyst, no such selectivity was observed. The rate of hydrogen uptake was nearly the same in both cases of 10- and 2-undecenoic acid. When synthetic vinyl polymer-protected platinum clusters (Pt-PVP) were used, the rate of hydrogenation was also independent of the location of a double bond in the substrate. Figure 7 shows the hydrogenation of the same substrates over the vinyl polymer-protected platinum cluster catalyst. Almost the same catalytic activities are shown for the hydrogenation of both 10- and 2-undecenoic acid.

When the corresponding sodium salts were used as substrates, however, the hydrogenation rate depended on the location of the double bond. The initial rates calculated from Figs. 5, 6, and 7 are summarized in Table 5, together with the regioselectivity, indicated by the ratio of the initial rates for 10- and 2-undecenoic acid (R_{10}/R_2). This table clearly demonstrates the different features in regio-selectivity between the surfactant- and polymer-protected colloidal cluster catalysts, as well as between free carboxylic acid and sodium carboxylate as substrates.

Discussion

Formation and Stabilization of Colloidal Dispersion of the Cluster Particles. Hydrophobic colloids, like colloidal platinum particles, can not be stably dispersed without protective colloids, like water-soluble polymers. The protective colloid generally stabilizes the colloidal particle in an aqueous solution, forming a sphere that includes a hydrophobic colloidal particle inside the protective colloids by a hydrophobic interaction. The spheres are thus stably dispersed in water. In the surfactant system, micelles are formed when the concentration of the surfactant is above cmc. Thus, the hydrophobic ultrafine particles of noble-metal clusters are homogeneously dispersed by being surrounded by the inner core of the micelles, which comprise the hydrophobic alkyl chains of the surfactants.[11] In general, micelles are readily destroyed by a heat treatment of the solution, or by the addition of an organic solvent. This could be the reason why colloidal particles of platinum clusters could not be obtained by either the alcohol-reduction method nor the hydrogen- and the photo-reduction method at lower concentrations of the surfactant than the cmc. Homogeneous dispersions were sometimes obtained by photo-reduction, even below the cmc. This fact is satisfactorily explained by the stabilization of the dispersed particles by the surfactant molecules adsorbed on the surface of the colloidal particles. The adsorbed surfactant molecules probably make the hydrophobic particles temporarily dispersed in the aqueous solution. However, these colloidal dispersions were unsatisfactorily surrounded by the surfactant, resulting in easy precipitation in the course of time.

Photo-reduction seems to be more suitable than does hydrogen-reduction in order to prepare ultrafine particles of noble-metal clusters under the present conditions. The photo-reduction method is often applied to the deposition of noble metals on the surface of a semiconductor to prepare a photocatalyst for solar energy conversion.[12] Although its reduction mechanism may be different from that of the semiconductor system, photoirradiation is a method with sufficient ability to reduce noble-metal ions to zero-valent metal clusters. Thus, ultrafine particles could be produced in the presence of protective colloids, like surfactants or polymers. The formation of monodispersed metal clusters can be interpreted as nucleation from a supersaturated dispersion of hydrophobic zero-valent metal atoms.[13] The difference in particle size between the two methods of reduction is attributable to the different concentration of zero-valent metal nuclei produced during the initial step. In other words, visible-light irradiation seems to produce larger amounts of uniform nuclei than hydrogen gas by the reduction of metal ions, resulting in smaller size and narrower size distribution of the particles produced. In contrast, the fact that hydrogen-reduction produces relatively large, widely distributed particles might be attributed to the smaller degree of supersaturation, because of the diffusion of gaseous hydrogen into the aqueous solution, which could result in a nonuniform growing of platinum particles.[13] That might be the reason why photo-reduction is superior to hydrogen-reduction from the aspects of small size and narrow size distribution.

The reionization of palladium clusters by oxidation under air, as shown in Fig. 2, provides evidence that the surfactant micelle has only the function to form homogeneous dispersion, but an insufficient function to protect metal clusters from oxidation. The palladium clusters produced by the alcohol-reduction are stable in an alcohol–water solvent, even under open air.[6] This is probably because of the reductive environment by the coexisting excess alcohol. In the present case, since the palladium atom is known to be more readily oxidized than platinum (standard redox potentials of $PdCl_4^{2-}/Pd$ and $PtCl_6^{2-}/Pt$ are −0.58 and −1.858 respectively.),[14] palladium clusters kept in the absence of such reductive agents as alcohol are readily oxidized to palladium ions by oxygen in the air.

Hydrogenation of Olefins. The catalytic activity of the colloidal dispersions of metal clusters depends on the method of preparation: That is, micelle-protected metal clusters prepared by photoirradiation have higher activity than the others. This phenomenon seems to be due to the fact that photo-reduced metal clusters are the smallest in size and have the largest effective surface area among those examined. Table 4 clearly indicates this trend regarding the effect of the size of platinum clusters on the catalytic activity.

In addition to the particle size, some other factors seem to influence the catalytic activity. Thus, the catalytic activities seem to be dependent upon the type of protective colloid, as is shown in Table 4. Among the platinum clusters prepared by the photo-reduction in the present study, the nonionic surfactant-protected one (Pt- $C_{12}EO$) was the most active, in spite of almost the same particle size. The electric charge of the hydrophilic groups in surfactants seems to have nothing to do with the reactivity since the substrate used has no charge by itself. The high catalytic activity in a nonionic surfactant system is supposed to be attributed to the ability of a micelle to solubilize hydrophobic substrates.[11] In addition to the protection of colloidal particles, the surfactant micelle has the function to solubilize the hydrophobic substrates into micelles so as to help their approach to the active site on the surface of the platinum clusters in the hydrophobic core of a micelle. Nonionic surfactants having polyethylene glycol moieties usually show an extremely lower cmc than do anionic or cationic surfactants; the hydrophobic substances are thus more easily captured by the minimum amount of the surfactant molecules. This fact results in a stable solubilization of vinyl acetate.

Figure 8 shows the substrate concentration dependence of the initial rate of hydrogenation by palladium clusters protected by nonionic surfactants. The apparent reaction rate initially increases with incresing concentration of the substrate, but gradually decreases after the substrate concentration reaches 0.1 $mmol\,dm^{-3}$. This result indicates that the substrates which react with hydrogen molecules are those solubilized by micelles at a low substrate concentration: that is, only the olefins solubilized by the micelles protecting the colloidal cluster catalysts can be hydrogenated in the present system. At a high substrate concentration, however, a considerable amount of the substrate is adsorbed on the surface of the micelle, or forms mixed micelles with nonionic surfactants; finally, the micelles may be destroyed. In fact, the micellar solution become turbid upon the addition of a considerable amount of the substrate.

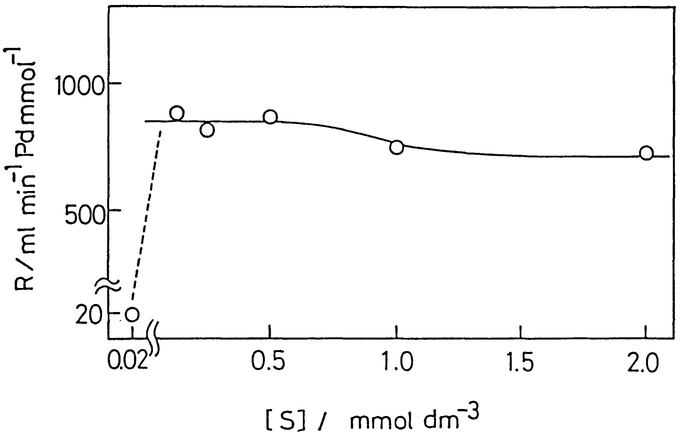

Fig. 8. Substrate concentration dependence of the initial rate of the hydrogenation of vinyl acetate catalyzed by palladium clusters protected by the nonionic micelles. $[C_{12}EO]=100$ mmol dm^{-3}, $[Pd]=0.2$ mmol dm^{-3}.

Regioselectivity in the Hydrogenation of Unsaturated Fatty Acids. The regioselectivity observed in the present hydrogenation of unsaturated fatty acids suggests the following mechanism for hydrogenation in a micellar solution. The fatty acid molecule comprises a hydrophobic alkyl chain and a hydrophilic carboxyl group at the end, and is known to form a Langmuir–Blodget film. It is thus reasonable to consider that the carboxyl groups of fatty acids solubilized by a micelle are stably located at a hydrophilic layer of the micelle. Since a relatively oriented environment is produced by the surfactant micelle, as shown in Figs. 9(a) and (b), it is most probable that the alkyl chain of the substrate molecule is placed in parallel to the alkyl chains of the surfactant molecules. Under these conditions, the C=C bond in 10-undecenoic acid is always placed near the platinum cluster and is readily hydrogenated on the surface of the cluster particle (Fig. 9(a)). In the case of 2-undecenoic acid and oleic acid, the double bonds of both substrates are located at the same distance from the methyl end groups of the corresponding alkyl chains, and seem to be under similar hydrophobic conditions, resulting in almost the same probability to encounter the active site of a platinum particle (Fig. 9(b)). The substitution of carboxylic acid with sodium carboxylate in the fatty acid did enhance the regioselectivity, as is shown in Table 5. This result can again support the hydrogenation reaction mechanism controlled by the reaction field produced by the micelles. The regio-selectivity regarding the initial rate of hydrogenation in the present study seems to have originated from this relatively highly oriented reaction field produced by the micelle.

In the case of metal clusters protected by the linear polymer, however, the reaction field made by the polymer is not as ordered as is the micellar system, because of the random molecular motion, which could be illustrated as Fig. 9(c). The double bond of 2-undecenoic acid seems to be easier to approach on the surface of the platinum cluster particle in the linear polymer than in the case of the a micellar system. This is why the catalytic activity of polymer-protected platinum cluster is independent of the location of a double bond in the substrate of fatty acid.

The difference in the regioselectivity between the surfactant and the polymer system could demonstrate the following reaction mechanism. The solubilization of hydrophobic substrates by a micelle or polymer is presumably the first step of a hydrogenation, which helps substrates approaching toward the surface of the platinum cluster particles. Then, the C=C double bonds are easily hydrogenated over the active sites of the cluster particles. The results of higher catalytic activity and regioselectivity in the case of Pt–$C_{12}EO$ than the other catalysts can be explained by this reaction mechanism. This hydrogenation model can be supported by the results regarding the hydrogenation of sodium salts of the corresponding unsaturated fatty acids shown in Table 5. When water-soluble sodium salts were used, the regioselectivity was observed, even in a system of poly(vinylpyrrolidone). Since the fatty acid substrates become surface active upon the introduction of sodium ions, the substrates could form an oriented reaction field by themselves. This seems to be the reason why regioselectivity was observed even in the case of a linear polymer as a protective colloid when sodium undecenoate was used as the substrate instead of undecenoic acid.

In summary, the surfactant in the present system plays a role not only as a protective colloid of hydrophobic metal particles, but also as a producer of an integrated reaction field. The platinum cluster catalyst protected by the surfactant micelle can provide further functions due to the micelles. The catalyst proposed in the present investigations would be important as one of the multifunctional catalysts comprising of organic and inorganic materials, and could be expected to be applied to the various catalytic reactions of a hydrophobic

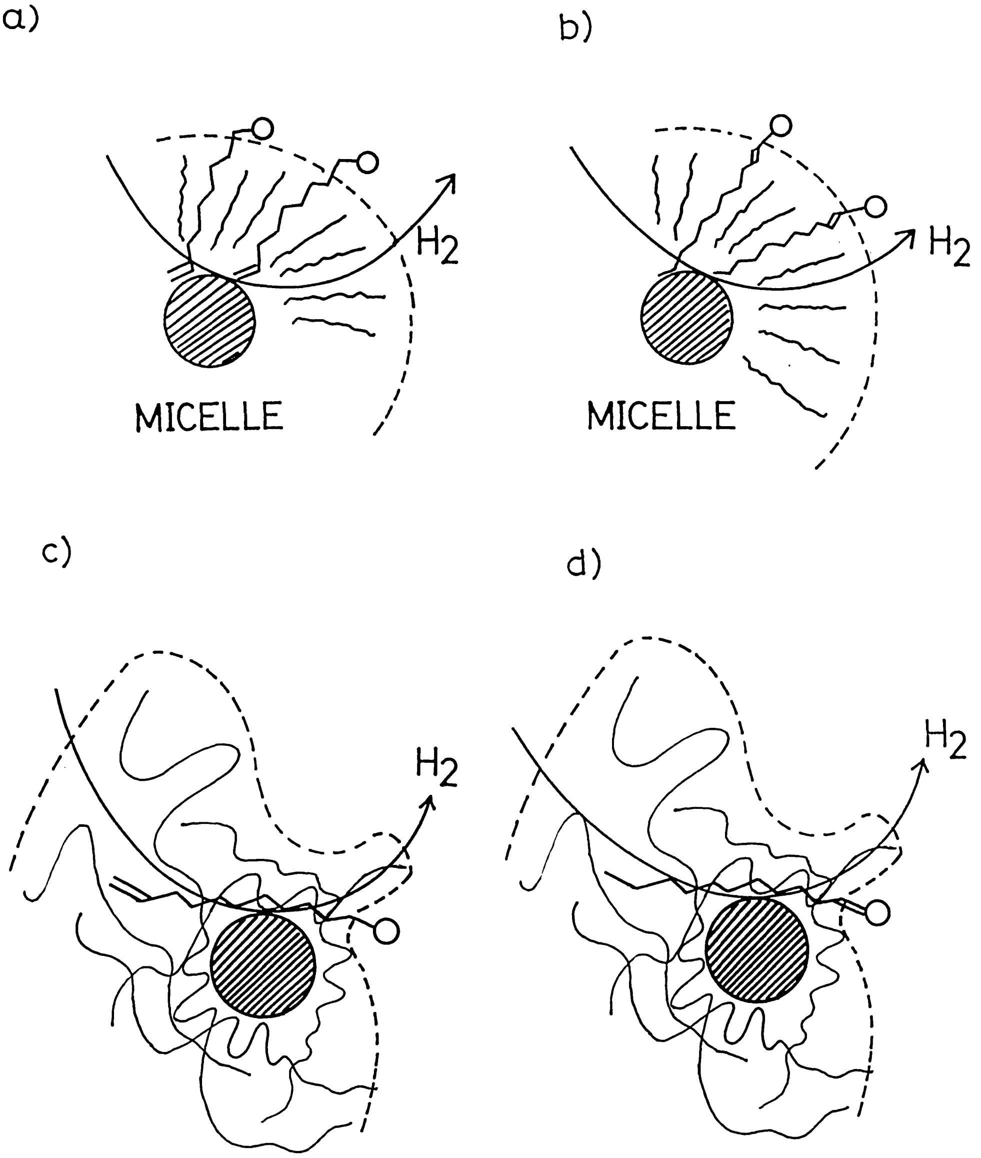

Fig. 9. Proposed mechanism for the hydrogenation of unsaturated fatty acids catalyzed by the colloidal platinum particles in a micellar system ((a) and (b)), and a polymer system ((c) and (d)).

substrate in an aqueous solution.

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