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Colloidal Noble Metal Catalysts Protected by Surfactant Micelles. Regio-Selectivity in the Hydrogenation of Unsaturated Fatty Acids in Organized Media

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Colloidal dispersions of platinum and palladium protected by nonionic surfactants were prepared by photo-irradiation. They work as active catalysts for the hydrogenation of unsaturated fatty acids and their sodium salts. The regio-selectivity was observed in the hydrogenation in the organized media which surround the colloidal particles. Thus, 10-undecenoic acid was more rapidly hydrogenated than 2-undecenoic acid.

The organized molecular assemblies like micelles have been paid much attention to these days with the interest of the specific environment formed by them. The micelle, which is microscopically heterogeneous and forms organized media, is often applied to various specific reactions. For example, micelles work as enzyme model catalysts in organic synthesis,[1,2] and carry out special reactions in photo-, and electro-chemical reactions.[3,4] Thus, the surfactants added to a reaction system can form micelles and result in acceleration of reactivity and increase of selectivity.

Noble metals are often used for the catalysts for various organic reactions. Especially the colloidal noble metals (dispersions of ultrafine particles) are interesting not only because of high activity due to large surface area, but also because of different selectivity from ordinary metal catalysts. The colloidal noble metals are prepared in the presence of some protective materials which solubilize hydrophobic colloids in an aqueous solution.[5-7] Recently we have reported about the preparation of colloidal platinum dispersions protected by surfactant micelles by using a photo-reduction method.[8,9] The surfactant micelle in this system plays the role not only of a protective agent, but also a producer of the reaction field. The micelles modified by ultrafine particles of noble metal are expected to work as a highly active and selective catalyst in conventional reactions which are catalyzed by noble metals. In this communication, colloidal platinum and palladium dispersions protected by surfactant micelle were prepared by a photo-reduction method, and their catalytic activities were examined. In hydrogenation of unsaturated fatty acids over the micelle-protected colloidal metal catalysts, the initial reaction rate depends on location of the double bond in a substrate molecule. This effect seems to be originated from the oriented structure of the hydrophobic core of the micelles.

Colloidal noble metals were prepared in the presence of polyethylene glycol monolaurate ($C_{12}EO$), a nonionic surfactant, and poly(N-vinyl-2-pyrrolidone) (PVP), a water-soluble polymer, by photo-irradiation in the same way as described in the previous paper.[8,9] An aqueous solution of hexachloroplatinic acid (2×10^{-4} mol dm^{-3}), and $C_{12}EO$ or PVP (1×10^{-1} mol dm^{-3}) was degassed and photoirradiated with 500 W super high pressure mercury lamp with a Pyrex filter until the solution turned brownish. The photo-reduction was also applicable for palladium ion, but, since palladium chloride was scarcely soluble in pure water, an appropriate amount of hydrochloric acid was added to the aqueous solution in order to dissolve it. The hydrogenation of unsaturated fatty acids, 10-undecenoic acid (10-C'_{10}COOH) and 2-undecenoic acid (2-C'_{10}COOH), was carried out in the following manner. The substrates used in this study are shown in Fig. 1. The water-soluble sodium salts, sodium 10-undecenoate (10-$C'_{10}COO^-$) and sodium 2-undecenoate (2-$C'_{10}COO^-$), which were prepared by neutralization of the corresponding acid with sodium hydroxide in ethanol, were also examined in this study. Ten cm^3 of the colloidal metal solution (2×10^{-4} mol dm^{-3}) was kept under

$CH_2=CH(CH_2)_8COOH$	10-C'_{10}COOH
$CH_2=CH(CH_2)_8COO^-Na^+$	10-$C'_{10}COO^-$
$CH_3(CH_2)_7CH=CHCOOH$	2-C'_{10}COOH
$CH_3(CH_2)_7CH=CHCOO^-Na^+$	2-$C'_{10}COO^-$

Fig. 1. Structures of the substrates for hydrogenation.

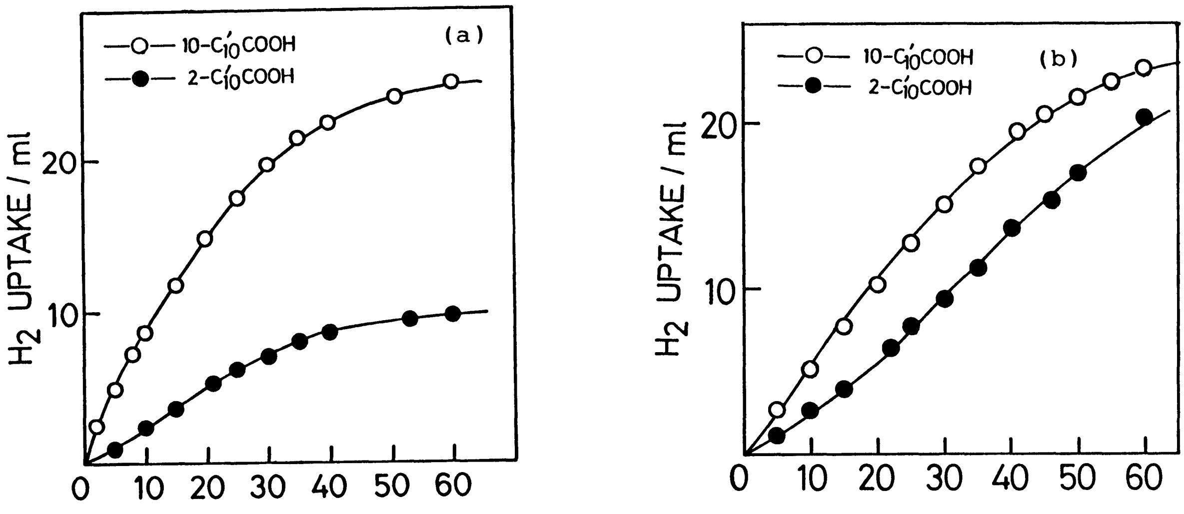

Fig. 2. Rate of hydrogen uptake in the hydrogenation of unsaturated fatty acids catalyzed by colloidal palladium dispersions protected by nonionic surfactant (a), and water-soluble polymer (b). See Fig. 1 for abbreviation.

a 1 atm hydrogen atmosphere until no further hydrogen gas was absorbed. Then, 1.0 mmol of the substrate was added to the solution. The rate was determined from the amount of hydrogen uptake measured by a gas burette, since the products confirmed by gas chromatography was only undecanoic acid without any byproduct and the amount of the product was consistent with the consumed hydrogen.

The examples of initial hydrogen uptake profiles over colloidal palladium catalysts are shown in Fig. 2. These figures clearly demonstrate that the initial rate of the hydrogenation is dependent on the substrate, that is, on the location of a double bond in the substrate molecule. The initial rates of hydrogenation of unsaturated fatty acids over the colloidal noble metal catalysts are summarized in Table 1 with the regio-selectivity, which is shown by the ratio of the initial rate of 10- and 2-undecenoic acid (R_{10}/R_2). In the case of nonionic surfactant micelle-protected colloidal catalysts, there exists a great difference in initial rate between 10-undecenoic acid and 2-undecenoic acid. This phenomenon is characteristic in a surfactant-protected colloidal catalyst, and is not observed in the case of a polymer-protected colloidal catalyst. In a linear polymer system, the initial rate of hydrogenation of both substrates are almost the same in each catalyst of platinum and palladium, where their selectivity ratio of R_{10}/R_2 of them is around 1. In the micellar system, on the other hand, especially with palladium particles, 10-undecenoic acid is hydrogenated 5 times more rapidly than 2-undecenoic acid. This high selectivity is attributed to function of the micelle to solubilize water-insoluble substrates. Fatty acid is a hydrophobic substrate, but the carboxylic group is hydrophilic in the molecule. Thus, the unsaturated fatty acids are most stably solubilized in micelles, when the carboxylic groups exist near the hydrophilic outer layer of the micelles and, at the same time, the long alkyl chain of the substrate stands in parallel with

Table 1. Initial rates of hydrogen uptake in the hydrogenation of unsaturated fatty acids and their sodium salts catalyzed by 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] = 100 mmol dm^{-3} at 30 °C, p_H = 1 atm. See text for abbreviation.

b) See Fig. 1 for the abbreviation of the substrate. The initial rates with asterisk(*) were obtained by using the sodium salts (10-$C'_{10}COO^-$ and 2-$C'_{10}COO^-$) instead of free acids.

c) The ratio of initial rates of 10- and 2-undecenoic acid.

the alkyl chains of the surfactants which form the central core of the micelles. On the basis of the oriented structure like this, the C-C double bond of 10-undecenoic acid, would be near the surface of the colloidal particles which are located near the center of the micelles. This would make 10-undecenoic acid hydrogenated very rapidly, since active sites of the catalysts are located near the surface of the particles. In the case of 2-undecenoic acid, on the other hand, the double bond is located next to the carboxylic group and there are few chances when the double bonds come near the surface of the colloidal catalysts to be hydrogenated.

When sodium salts were used as substrates, the regio-selectivity was also observed as seen in the result of free fatty acids even in the case of polymer-protected colloidal catalyst. Since the sodium salts originally have high solubility in water and are surface active, the substrate molecules itself form micelle-like organized assemblies. Owing to this fact, a similar reaction field as the micellar system is formed by the surface active substrates in the hydrophobic domain of the protective polymer, resulting in the double bonds of sodium 2-undecenoate to stay apart from the surface of the colloidal particles. Thus, the initial rate of hydrogenation of sodium 2-undecenoate was extremely lower than that in the case of free fatty acid in the polymer system.

The obtained results seem to be originated from the organized reaction field produced by the surfactant micelles. This regio-selectivity is one of the evidence for the fact that hydrogenation takes place after the substrates are solubilized in micelle or polymer by hydrophobic interactions.

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