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# Colloidal Platinum Catalyst Protected by Nonionic Monomeric and Polymerized Micelle for Photochemical Hydrogen Generation from Water

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Colloidal dispersion of platinum protected by nonionic polymerized micelle was prepared by visible light irradiation followed by $\gamma$-ray polymerization of the aqueous solution of $H_2PtCl_6$ and polyethylene glycol undecenoate. The colloidal platinum thus obtained showed higher catalytic activity in photochemical hydrogen generation than that protected by the corresponding anionic polymerized micelle.

Solar photo-energy conversion is one of the attracting techniques to solve energy problems. An artificial photosynthesis system using tris(2,2'-bipyridine)-ruthenium(II) chloride ($[Ru(bpy)_3]Cl_2$) and methyl viologen ($MV^{2+}$) is being widely investigated with great interests.[1-4] In this system, hydrogen gas, which provides clean and renewable energy, is generated from water in the presence of colloidal platinum[5] or hydrogenase[6] by use of photo-energy. The present authors have already reported about the preparation of colloidal platinum in the presence of polymers,[7] micelles,[8] and anionic polymerized micelle.[9] The ultrafine platinum particles thus prepared act as stable and active catalysts for photochemical hydrogen generation. In the present communication, the colloidal platinum protected by nonionic polymerized micelle has been prepared. The effect of protective colloid for the catalytic activity has been investigated in view of the stability of the colloidal dispersion and the electrostatic interaction between the protective colloid and methyl viologen cation radical. The results have demonstrated that the colloidal platinum protected by nonionic polymerized micelle is the most active catalyst among those investigated.

Nonionic unsaturated surfactant having poly(ethylene glycol) moiety ($C'_{11}EO$) was synthesized in the following procedure. Poly(ethylene glycol) monomethyl ether (Aldrich, average molecular weight 550, 0.1 mol) and equimolar pyridine were dissolved in 100 $cm^3$ anhydrous tetrahydrofuran. Excess amounts of 10-undecenoyl chloride (Tokyo Kasei, purified by distillation under reduced pressure, 90 °C /2

$$CH_2{=}CH(CH_2)_8COCl + HO(CH_2CH_2O)_nCH_3 \xrightarrow[\text{THF, r.t.}]{\text{Py}} CH_2{=}CH(CH_2)_8COO(CH_2CH_2O)_nCH_3$$

$C'_{11}EO$ ($n \fallingdotseq 12$)

Torr) were added dropwise to the solution. The mixed solution was vigorously stirred on an ice bath for 3 h and continuously stirred overnight at room temperature. After pyridine hydrochloride was filtered off, the solvent was evaporated under reduced pressure. The obtained viscous liquid was dissolved in chloroform again and purified through an activated alumina column. The structure of the product was confirmed by $^1$H-NMR and IR spectra. Colloidal platinum was prepared from hexachloroplatinic acid in the presence of C'$_{11}$EO by the photo-reduction method which was previously reported.[8,9] Figure 1 shows the electron micrograph of colloidal platinum particles protected by nonionic polymerized micelle. The obtained colloidal particles were small and rather monodispersed. The average particle size was about 2.5 nm in diameter in the micrograph. The size was almost the same as those obtained by photo-reduction in previous cases.[8,9] The protective colloid was polymerized by γ-ray irradiation for 24 h at room temperature ( 0.14 Mrd $h^{-1}$ )[10] after preparing colloidal platinum in the presence of C'$_{11}$EO. Polymerization of C'$_{11}$EO was confirmed by GPC in a chloroform solution. The chromatogram shows that the average molecular weight is about 3000 from the standard of polystyrene. The protective colloid still involved less amount of unreacted monomeric surfactants. The yield of polymerized micelle was calculated to be 75% from the

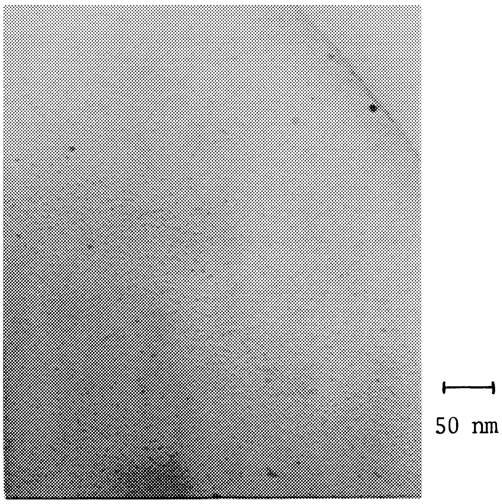

Fig. 1. Electron microgragh of colloidal platinum particles protected by nonionic polymerized micelle.

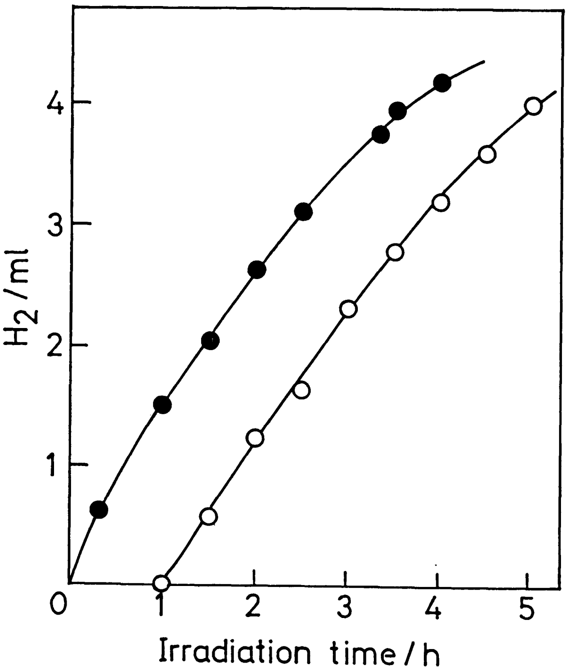

Fig. 2. Photochemical hydrogen generation catalyzed by colloidal platinum catalysts protected by nonionic monomeric micelle (Pt-MC$_{12}$EO, ● ), and nonionic polymerized micelle (Pt-PC'$_{11}$EO, ○ ).

area ratio in the chromatogram.

Photochemical hydrogen generation studies were performed by the following manner. Ten milliliter of the mixed solution made up of $[Ru(bpy)_3]^{2+}$ ($5 \times 10^{-5}$ mol $dm^{-3}$), $MV^{2+}$ ($5 \times 10^{-3}$ mol $dm^{-3}$), EDTA•2Na ($5 \times 10^{-2}$ mol $dm^{-3}$), and colloidal Pt ($5 \times 10^{-5}$ mol $dm^{-3}$) was photoirradiated under argon atmosphere by a 500W super high pressure mercury lamp ($\lambda$ >390nm by cut filter) at 25 °C, and the evolved gas was characterized by gas chromatography (molecular sieves 13X). The catalytic activities were compared with the other colloidal platinums by an initial rate of the hydrogen generation. Figure 2 shows the amount of the generated hydrogen gas using colloidal platinum catalyst protected by nonionic monomeric micelle ($MC_{12}EO$) and polymerized micelle ($PC'_{11}EO$). The induction period in the polymerized micelle-protected colloid seems to be due to the consumption of hydrogen by hydrogenation of nonpolymerized undecenoate moieties contaminated in the polymerized micelle.

In the previous communication, we reported that polymerized micelle-protected colloidal platinum was more active than monomeric micelle-protected one in the case of anionic protective colloid.[9)] In the present case, however, monomeric micelle-protected colloidal platinum showed almost the same catalytic activity compared with the one protected by polymerized micelle. This fact might be attributed to the difference in stability between nonionic and anionic micelle. Colloidal platinum protected by anionic monomeric micelle was so unstable because of the ionic interaction with the other ionic species in the reaction system that the colloidal solution turned microscopically inhomogeneous under the reaction conditions. The present nonionic surfactant ($C_{12}EO$) has lower critical micellar concentration than anionic sodium undecanoate and less interaction with ionic species. So it is still stable and homogeneous under the reaction conditions in spite of monomeric micelle.

Catalytic activities of various colloidal platinums are collected in Table 1 with relative activity using that of Pt-poly(N-vinyl-2-pyrrolidone) (Pt-PVP) as a standard (100). This Table clearly indicates that protective colloid plays an important role for the catalytic activity of colloidal platinum for photochemical hydrogen generation. Nonionic protective colloid seems to be more suitable than

Table 1. Catalytic activities of colloidal platinum catalyst for photochemical hydrogen generation in the system of $EDTA/Ru(bpy)_3^{2+}/MV^{2+}$

| Pt-catalyst[a)] | State of protective colloid | Relative activity[b)] |
|---|---|---|
| $Pt\text{-}PC'_{11}EO$ | nonionic polymerized micelle | 306 |
| $Pt\text{-}MC_{12}EO$ | nonionic monomeric micelle | 302 |
| $Pt\text{-}PC'_{10}COO^-$ | anionic polymerized micelle | 105 |
| Pt-PVP | nonionic linear polymer | 100 |

a) See text for abbreviation.

b) Initial rate of hydrogen generation using that of Pt-PVP as a standard(100).

the anionic protective colloid, poly(sodium undecenoate) ($PC'_{10}COO^-$). In nonionic systems, interactions between methyl viologen and protective colloid are so small that there are few interference for methyl viologen with getting into the inner core of protective colloid and approaching to the surface of colloidal platinum particles. On the other hand, in an anionic system, methyl viologen cation radicals might strongly interact with anionic surface of the protective colloid, and be accumulated around the protective colloid with electrostatic forces. This effect prevents methyl viologen cation radicals to enter the inner core approaching the platinum surface. And further more, the solution becomes microscopically heterogeneous by ionic complex formation of anionic surfactants with cationic species such as $MV^{2+}$ or $Ru(bpy)_3{}^{2+}$. So methyl viologen cation radicals are readily deactivated by reverse electron transfer from methyl viologen cation radicals to nearby $Ru(bpy)_3{}^{3+}$.

The Pt-$PC'_{11}$EO colloidal catalyst showed three times higher activity than Pt-PVP colloid. This result can be explained in terms of the ability of charge separation and stability of colloidal platinum. Methyl viologen becomes relatively hydrophobic when it changes to cation radical by capturing an electron from photoexcited $Ru(bpy)_3{}^{2+}$. This hydrophobic cation radicals can readily be captured by the hydrophobic inner core of the polymerized micelle. So $MV^{+\cdot}$ exists in the different site from $Ru(bpy)_3{}^{3+}$ and the reverse electron transfer seems to be restrained by this charge separation effect. In linear polymer system like PVP, on the other hand, an effect of solubilizing hydrophobic substances in an aqueous solution seems to be less than that in the micellar system. And hydrophobic platinum particles are also more stable in micelles than in linear polymers. Both effects are the reason why the colloidal platinum protected by nonionic polymerized or monomeric micelle is more active as a catalyst than that protected by PVP.

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