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COLLOIDAL PLATINUM CATALYST FOR LIGHT-INDUCED HYDROGEN EVOLUTION FROM WATER. A PARTICLE SIZE EFFECT

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Well-dispersed fine and stable colloidal platinum is easily prepared by refluxing the solution of chloroplatinic acid in alcohol (and water) in the presence of poly(vinyl alcohol) or polyvinylpyrrolidone under air. The catalytic activity of the colloidal platinum for light-induced hydrogen evolution from water depends on the particle size of the platinum indicating the maximum activity for the colloid of about 30 Å in diameter.

There has been an increasing interest recently in the light-induced hydrogen evolution from water with photocatalytic system.1) Formation of hydrogen is a half reaction of the photochemical water splitting, which is important for a means of solar energy conversion and storage.2) Platinum oxide, especially colloidal platinum, has got much attention as a catalyst for an electron transfer process resulting in hydrogen evolution from proton in a homogeneous system.3-17) On comparison with platinum oxide, the colloidal solution of platinum has advantages of high activity on the basis of the amount of platinum used, and good transparency of the irradiated system. The effects of the particle size on the efficiency of hydrogen generation are discussed recently. In one report,18) colloidal platinum having particle radii of 110 Å was claimed to be exceptionally active in promoting hydrogen evolution from water. A systematic study by another group19) concerning particle size effects on methyl viologen-mediated photochemical hydrogen generation, however, indicates no net size effect over a wide range.

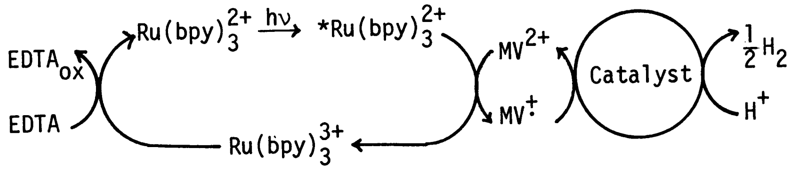
We have investigated on the fine colloidal dispersions of transition metals as the catalysts for selective hydrogenation of olefins and dienes.20) Our colloidal transition metals can be very easily prepared. They are stable in solution for several months, and very effective as the catalyst for hydrogenation reaction. We wish to report here the application of our method to preparation of colloidal platinum indicating the high efficiency as the catalyst for hydrogen evolution from water and the size effect of the platinum particles on the catalytic efficiency.

Colloidal solution of platinum was prepared by reduction of chloroplatinic acid with alcohol by the similar way to that for preparation of colloidal rhodium[20,21] or palladium.[20,22] The preparative procedures for colloidal platinum are as follows. Poly(N-vinyl-2-pyrrolidone) (PVP, degree of polymerization 3250, Tokyo Kasei Kogyo Co., Ltd., 150 mg, 1.35 mmol as monomeric residue) or poly(vinyl alcohol) (PVA, degree of polymerization 500, Nippon Synthetic Chem. Ind. Co., Ltd., 150 mg, 3.33 mmole) and chloroplatinic acid (Kojima Chem. Co., Ltd., 17.1 mg, 0.033 mmol) were dissolved in an alcohol(25 ml)-water(25 ml) mixed solvent to form a yellow solution. Refluxing the solution under air for 1.5 hr gave a homogeneous dark brown solution of colloidal dispersions of platinum. The colloidal dispersions are also prepared by dropwise addition of an ethanol solution (5 ml) of sodium hydroxide (6.7 mg, 0.17 mmol) to the solution under reflux.

The colloidal solution of platinum was characterized by the electron microscopy. The sample films prepared by evaporation of a small amount of the colloidal solution to dryness on a collodion film which was coated with a carbon layer and supported on copper grids were mounted in an electron microscope, Hitachi Model H-500, operated at 125 kV. The magnification of the electron microscope was 100,000. The diameter of each of the platinum particles, in arbitrarily chosen areas of $6 \times 10^{-6} Å^2$, was determined from the enlarged photographs, which correspond to a magnification of 260,000. The particle size distribution and the average diameter of platinum particles were obtained on the basis of these results.

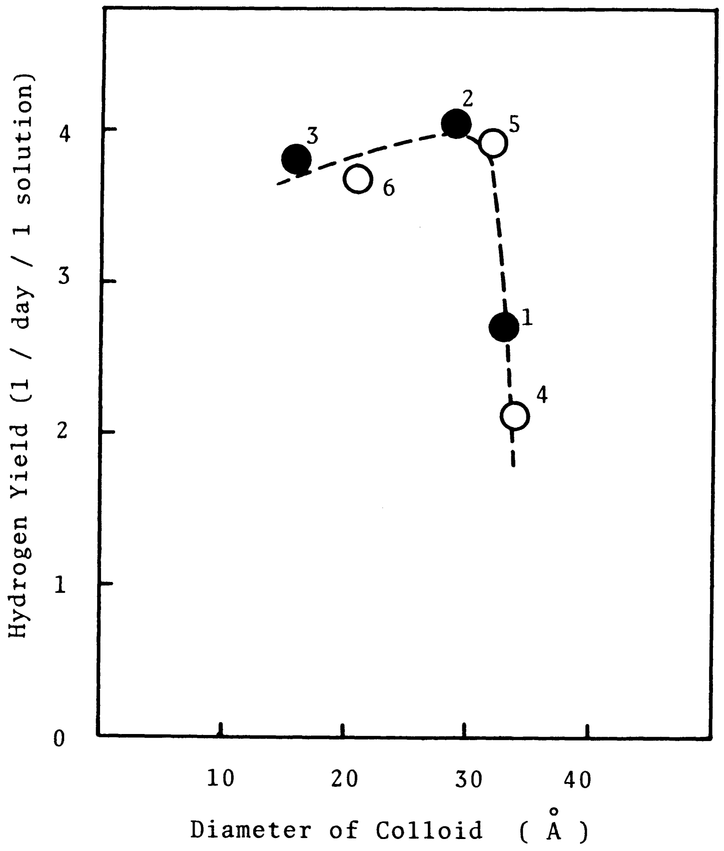
Tris(bipyridine)ruthenium(II) dichloride ($Ru(bpy)_3^{2+}$) as a photosensitizer, methyl viologen dichloride (MV^{2+}) as an electron mediator, and ethylenediamine tetraacetic acid (EDTA) as an electron source were chosen for photocatalytic hydrogen evolution experiments. The mechanism of hydrogen evolution in this photocatalytic system has been well established as shown in Scheme 1, where $EDTA_{ox}$ shows the oxidized state of EDTA.[1]

Scheme 1.



A typical experiment was performed under nitrogen as follows. An aqueous solution (20 ml) containing 5.0×10^{-5} M of $Ru(bpy)_3^{2+}$, 5×10^{-2}M of MV^{2+}, 5×10^{-2} M of EDTA·2Na, and 6.6×10^{-5} M of colloidal platinum was placed in a Pyrex Schlenk tube fitted with a septum. The aqueous solution was degassed by freeze-thaw cycles, filled with pure nitrogen, and irradiated with an Ushio 500W super high pressure mercury lamp with a Toshiba UV-39 cut off filter (> 390 nm) for an hour with being stirred with a magnetic stirrer. There appears the intense blue color of methyl viologen radical cation ($MV^{+\cdot}$)in about 5 min irradiation and the color is kept during the irradiation. A portion of evolved hydrogen was taken through the septum with an air-tight syringe and analyzed by GLPC (Porapak Q, 2 m, 30°C). The gas phase also contain carbon dioxide, the decomposition product of EDTA.

The hydrogen evolution rates depend on the catalysts used. The largest rate among the present experiments was obtained with the catalyst of colloidal platinum



Fifure 1. Correlation between the Yields of Hydrogen in a $Ru(bpy)_3^{2+}/MV^{2+}/EDTA$ System and the Diameter of Platinum Particles of Catalysts.

Catalyst:

(1) Pt-PVP-MeOH / H_2O
(2) Pt-PVP-EtOH / H_2O
(3) Pt-PVP-EtOH / NaOH
(4) Pt-PVA-EtOH / H_2O
(5) Pt-PVA-EtOH / H_2O,NaOH
(6) Pt-PVA-MeOH / H_2O

prepared by refluxing in the presence of polyvinylpyrrolidone in an ethanol-water mixed solvent (Pt-PVP-EtOH/H_2O). The hydrogen evolution rates with the different type of colloidal platinum catalysts were plotted in Figure 1 against the average diameters of particles of colloidal platinum, determined from the electron micrograph. The abbriviations of catalysts in Figure 1 are the same way with that of Pt-PVP-EtOH/H_2O. In fact, the hydrogen evolution rate depends on the size of colloidal particles of platinum, which has the optimum diameter of about 30 Å. The similar curves were obtained in both series of catalysts prepared in the presence of PVP(●) and PVA (○) as shown in Figure 1. If the hydrogen evolution rate would depend on the surface area of catalyst, the rate should increase with decrease of an average diameter. The present results might suggest that the particle size of 30 Å is necessary for the platinum particle to be simultaneously or closely attacked by two molecules of $MV^{+\cdot}$ and/or to reserve two electrons for some time until the electrons migrate from the particle to two protons on the surface to generate a hydrogen molecule.

The hydrogen evolution rate depends also on the amount of platinum catalyst and pH of the irradiated solution. The optimum conditions are about 0.07 mM and pH 6, respectively, in the present system. The details will be discussed in a full paper.

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