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Comparison of Hydrogenase and Colloidal Platinum as Photo-induced Hydrogen Evolution Catalysts

ICHIRO OKURA and SHIN KUSUNOKI

Department of Chemical Engineering, Tokyo Institute of Technology, Meguro-ku, Tokyo, 152, Japan

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Various attempts have been made to develop suitable redox systems for photochemical utilization of solar energy. Recent work [1] has shown that three component systems containing a photosensitizer, an electorn donor and an electron acceptor can be used to evolve hydrogen when a suitable catalyst is present. The catalysts employed almost exclusively in these studies are hydrogenase and platinum. As we reported previously [2] the turnover number per active site of hydrogenase was 500 times larger than that for colloidal Pt at the initial stage of the reaction. In practice, however, the catalyst should be not only highly active, but also suitable for long-term use. In this letter, time dependences of activities for hydrogen evolution of hydrogenase and colloidal Pt were compared and the deactivation mechanism of colloidal Pt is discussed.

Experimental

All reagents were obtained from commercial sources and were of the highest purity available. Zinc-mesotetraphenylporphyrintrisulfonic acid (Zn-TPPS$_3$) was synthesized according to ref. 3. Hydrogenase from *Desulfovibrio vulgaris* was purified according to Yagi's method [4]. Colloidal Pt was prepared by the reduction of chloroplatinic acid with sodium citrate [5]. The Pt sol thus prepared has been found by electron microscopy to have particles with an average diameter of 34 Å with deviation from the mean of 25% [5].

A typical experiment was performed as follows under anaerobic conditions. Six milliliters of the solution containing methyl viologen (7.14×10^{-6} mol), mercaptoethanol (1.63×10^{-3} mol), Zn-TPPS$_3$ (6.18×10^{-9} mol) and hydrogenase (4.42×10^{-11} mol) or colloidal Pt (3.75×10^{-8} mol) in a Pyrex reactor were irradiated wtih light from a 150 W tungsten lamp. Light of wavelength less than 390 nm was cut off by a Toshiba L-39 filter. The evolved hydrogen was collected by a sampling valve and analyzed by g.l.c.

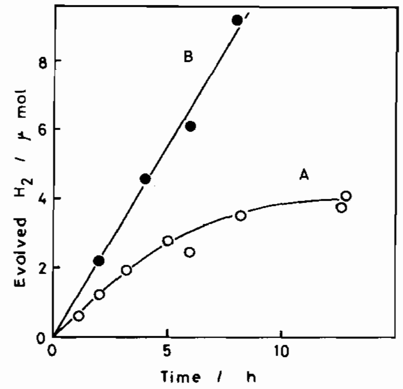

Fig. 1. Time dependence of hydrogen evolution with hydrogenase (B) and with colloidal Pt (A).

Results and Discussion

The time dependences of photo-induced hydrogen evolution of hydrogenase and colloidal Pt are shown in Fig. 1. In these experiments the concentration of the reduced form (MV$^+$) of methyl viologen was kept constant during the reaction to make the rate-determining step of this reaction to be the proton reduction step by MV$^+$.

In the case of hydrogenase, hydrogen evolved linearly with time and no deactivation of hydrogenase was observed within 24 hours. On the other hand, the hydrogen evolution rate gradually decreased in the case of colloidal Pt (curve A).

The causes for the rate decrease are considered to be colloidal Pt coagulation and/or the decrease of the effective concentration of methyl viologen by hydrogenation of MV$^+$ by hydrogen produced with colloidal Pt, for Johansen *et al.* [6] and Keller *et al.* [7] have reported that colloidal Pt is active for MV$^+$ hydrogenation. However, the spectrum at 256 nm, which is characteristic for the hydrogenation product of MV$^+$, was not observed in the experimental conditions and no decrease of the MV$^+$ concentration was observed and it was kept constant during the reaction. From the above results it is concluded that the rate decrease is not caused by MV$^+$ hydrogenation but coagulation of colloidal Pt.

To elucidate the cause of the rate decrease, the amounts of hydrogen evolved with various concentrations of colloidal Pt were compared as shown in Table I.

If the activity of colloidal Pt decreases by 1st order or 2nd order decay, the reaction rates, V, should be expressed as follows, respectively.

TABLE I. Photo-induced Hydrogen Evolution after 2 h and 6 h with Colloidal Pt (see text for reaction conditions).

Amounts of Pt introduced	Evolved H_2 for 2 h	Evolved H_2 for 6 h	n_{2h}/n_{6h}
2.54×10^{-8} mol	3.07×10^{-6} mol	5.98×10^{-6}	0.51
5.08×10^{-8}	6.60×10^{-6}	9.38×10^{-6}	0.70
7.63×10^{-8}	5.82×10^{-6}	8.86×10^{-6}	0.66
1.02×10^{-7}	1.10×10^{-5}	1.62×10^{-5}	0.68
1.27×10^{-7}	1.29×10^{-5}	1.86×10^{-5}	0.70
1.53×10^{-7}	1.46×10^{-5}	1.90×10^{-5}	0.77

$$V = A[\mathrm{Cat}]_o e^{-kt} \qquad \text{(1st order decay)}$$

$$V = \frac{A'[\mathrm{Cat}]_o}{1 + k't[\mathrm{Cat}]_o} \qquad \text{(2nd order decay)}$$

where k, k′ are decay constants and $[\mathrm{Cat}]_o$ is the initial concentration of colloidal Pt. The ratio of the amounts of hydrogen produced at different reaction periods are expressed as follows.

$$\frac{n_t}{n_{t'}} = \frac{1 - e^{-kt}}{1 - e^{-kt'}} \qquad \text{(1st order decay)}$$

$$\frac{n_t}{n_{t'}} = \frac{\ln(kt + 1/[\mathrm{Cat}]_o)}{\ln(kt' + 1/[\mathrm{Cat}]_o)} \qquad \text{(2nd order decay)}$$

where n_t and $n_{t'}$ are the amounts of hydrogen produced at time t and t′, respectively. If colloidal Pt is deactivated by 1st order decay $n_t/n_{t'}$ should be constant. If it is deactivated by 2nd order decay $n_t/n_{t'}$ should depend on the initial concentration of colloidal Pt.

As shown in the Table, $n_t/n_{t'}$ was almost constant and did not depend on the initial concentration of colloidal Pt. So, the activity of colloidal Pt decreases by 1st order decay, indicating that the deactivation may be caused by the coagulation upon collision of colloidal Pt and other molecules.

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