Photocatalyzed Production of Hydrogen and Iodine from Aqueous Solutions of Iodide Using Platinum-Loaded TiO_2 Powder

Teruhisa Ohno, Susumu Saito, Kan Fujihara, and Michio Matsumura*

Research Center for Photoenergetics of Organic Materials, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560

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Hydrogen evolution and oxidation of iodide on photoirradiated Pt-loaded TiO_2 powder were studied in the deaerated solutions containing iodide ions. These photocatalytic reactions have been considered to be difficult because the reaction is endothermic and reversible. However, we found that under some experimental conditions the reactions proceeded until the concentration of I_3^- ions reached a limiting level. The initial rate of the reactions and the limiting concentration of I_3^- ions in solution were enhanced as the pH of the solution decreased. In order to elucidate the pH dependence, the anodic current due to the oxidation of iodide ions on TiO_2 film electrodes and the adsorptivity of iodide ions on TiO_2 powder were measured. The results showed that the enhanced reactivity at low pH is due to the increased adsorptivity of iodide ions on TiO_2. It was also found that the electric contact between platinum and TiO_2 is important to make the reactions go forward.

In these years the conversion of light energy into chemical energy has evoked great interest with a view to creating new energy conversion and storage systems.[1—9] In the studies of this field, semiconductor particles are most commonly utilized as the photocatalysts, because the electrons and holes photogenerated in the semiconductor particles have strong reducing and oxidizing power, respectively.[5—9] Another advantage of the utilization of a semiconductor photocatalyst lies in the fact that the electrons and holes in the particles are separated efficiently by the energy band structure of semiconductors. Many useful chemical reactions have been studied by utilizing these advantages.[10—17]

The separation of the oxidation and reduction sites on the semiconductor photocatalysts is important to make the photocatalytic reaction go forward, because the oxidation and reduction proceed simultaneously on one particle. For this reason, platinum fine particles are usually deposited on semiconductor particles.[10—17] The platinum forms the reducing sites on which protons are usually reduced to hydrogen gas. To separate the oxidation and reduction sites on the photocatalysts, modification of semiconductor particles with different semiconductors has also been reported.[18,19]

Utilizing the advantages of the semiconductor photocatalysts, interesting photocatalytic reactions have been reported. Among them, efficient reactions are mostly chemically irreversible.[10,13] However, when we aim at constructing the energy converting and storing systems, the reactions should be endothermic and reversible. To promote such reactions on the semiconductor particles, the back reactions are the serious problem to be solved. The typical strategies to prevent the back reactions are 1) to remove the products out of the system by forming gaseous products,[20—22] 2) to introduce an oil/water interface to separate the products,[23] 3) to utilize a membrane to separate the products,[24] and 4) to design the structure of the catalysts using the layered crystals.[25,26]

In the present study, we aimed at the evolution of hydrogen from water using iodide ions as the electron donors. The oxidation of iodide ions on the photoirradiated TiO_2 particles in the aerated solutions has been reported by Draper and Fox.[27] Kormann et al.[28] have also reported the formation of the one-electron-oxidation intermediate I_2^- by photoirradiation of TiO_2 colloidal particles. Our reaction system is different from theirs in that we aim at the evolution of hydrogen in the deaerated solutions. From the results of our study, we report for the first time that hydrogen evolves on the photoirradiated Pt-loaded TiO_2 particles if one uses iodide ions as the electron donors under some experimental conditions. The results demonstrated that the pH of the solution and the contact between TiO_2 and platinum are important to make the reaction go forward.

Experimental

Materials. Titanium dioxide (TiO_2) powders obtained from Kanto Chemical Co. and the Catalyst Society of Japan (TIO-5) were used in this study. Some TiO_2 powders obtained from other sources were also tested in some experiments. The TiO_2 powder obtained from Kanto Chemical had the anatase form and its purity was above 99%. The TIO-5 powder had the rutile form with the purity above 99.9%. Platinum black powder was purchased from N. E. Chemcat. Co., Ltd. as a guaranteed reagent. Hydrogen hexachloroplatinate(IV) and potassium iodide were commercially obtained from Wako Pure Chemical Industries Ltd. Other chemicals used for experiments were purchased from commercial sources as guaranteed reagents and used without further purification.

Preparation of Pt-Loaded TiO_2 Photocatalyst. Platinum particles were loaded on TiO_2 powder by mixing TiO_2 powder (2.0 g) with 2 wt% platinum black powder in an agate mortar. Some of the Pt-loaded TiO_2 particles were next heated at 500 °C for 1 h under an aerated condition in an electric furnace for the purpose of improving the contacts between TiO_2 and platinum. The X-ray diffraction patterns of the TiO_2 powders showed that their crystal structures or the crystallinity did not change even after the heat treatment. For some experiments, platinum was loaded on TiO_2 by means of the photocatalytic reactions in the aqueous solution of hydrogen hexachloroplatinate(IV) using ethanol as the sacrificial electron donor. Scanning electron micrographs (SEMs) of the Pt-loaded TiO_2 powders were obtained using a Hitachi Model S-5000 microscope.

Photocatalytic Reactions. Photocatalytic reactions were carried out in a reaction cell containing an aqueous solution of 1.0 mol dm^{-3} potassium iodide (50 ml) and the Pt-loaded TiO_2 particles (200 mg). The oxygen dissolved in the solution was removed by the freeze-pump-and-thaw method. In order to chemically reduce platinum oxide, which was included in the platinum black powder, hydrogen gas was introduced into the reaction cell. After the introduction of hydrogen, the suspension was stirred for 1 h, and the excess hydrogen gas was removed by repeating the freeze-pump-and-thaw cycles again. After these processes, the photocatalytic reactions were carried out in vacuo in the closed cell containing the aqueous solution of 1 mol dm^{-3} potassium iodide. A 500 W high-pressure Hg lamp was used as the light source. The light beam was passed through a 1-cm water filter and a Pyrex glass filter to cut off the heat radiation and deep UV light of wavelengths shorter than 300 nm. The amounts of I_3^- ions produced by the photocatalytic reactions were determined from the UV-vis absorption spectra measured on a Shimadzu UV-2500PC spectrophotometer. The amounts of hydrogen evolved were measured using a JEOL JGC-20K gas chromatograph and an oil manometer. Evolution of small amounts of hydrogen was detected after the photoirradiation of the photocatalyst in the absence of potassium iodide. This reaction was due to the oxidation of the impurities included in the reaction cell. Hence, in the experiments for determining the amounts of evolved hydrogen, the impurities in the cell were eliminated by photoirradiation of the photocatalysts for about 10 h before the addition of iodide ions.

Electrochemical Oxidation of Iodide Ions on TiO_2 Film Electrodes. The electrochemical behavior of iodide ions on TiO_2 film electrodes was measured in the electrochemical cell having a Pt counter electrode and an Ag/AgCl reference electrode. The TiO_2 film electrodes, which were fabricated for the study of the Grätzel cell,[29)] were kindly supplied by Ishihara Sangyo Co., Ltd. In the electrodes, SnO_2-coated glass plates were used as the substrate. The apparent area of the TiO_2 films exposed to the solution was about 1.0 cm^2. Before the electrochemical measurements, oxygen in the solution was removed by bubbling high purity nitrogen gas. The potential of the TiO_2 film electrodes was controlled with a Nikko-keisoku potentiostat NPOT-2501.

Adsorptivity of Iodide Ions on TiO_2 Particles. For the evaluation of the amounts of iodide ions adsorbed on the surface of the photocatalyst, TiO_2 particles (100—200 mg) were added to the solution of potassium iodide (2.0 mol dm^{-3}) under deaerated conditions. The change of the concentrations of the iodide ions in the solution, which was caused by the adsorption on iodide ions on the TiO_2 particles, was monitored with a TOA I-125 iodide-ion selective electrode.

Results and Discussion

Photocatalytic Reaction on the Pt-Loaded TiO_2 Particles. SEM micrographs of typical photocatalysts used in this study are shown in Fig. 1. Figure 1a shows the structure of TiO_2 (Kanto Chemical) particles loaded with 2 wt% platinum particles by mixing them in an agate mortar. The structure after the heat-treatment at 500 °C for 1 h is shown in Fig. 1b. Although the photocatalytic activity was enhanced by the heat-treatment, as will be discussed later, no noticeable differences were observed between the structures of Figs. 1a and 1b. The Pt particles loaded on TiO_2 by the photochemical method were smaller than those loaded by the mechanical mixing. However, the photocatalytic activities were almost the same irrespective of the loading methods, as will be discussed later. In the present study, therefore, we mostly used the photocatalysts on which Pt powder was loaded by the mechanical mixing.

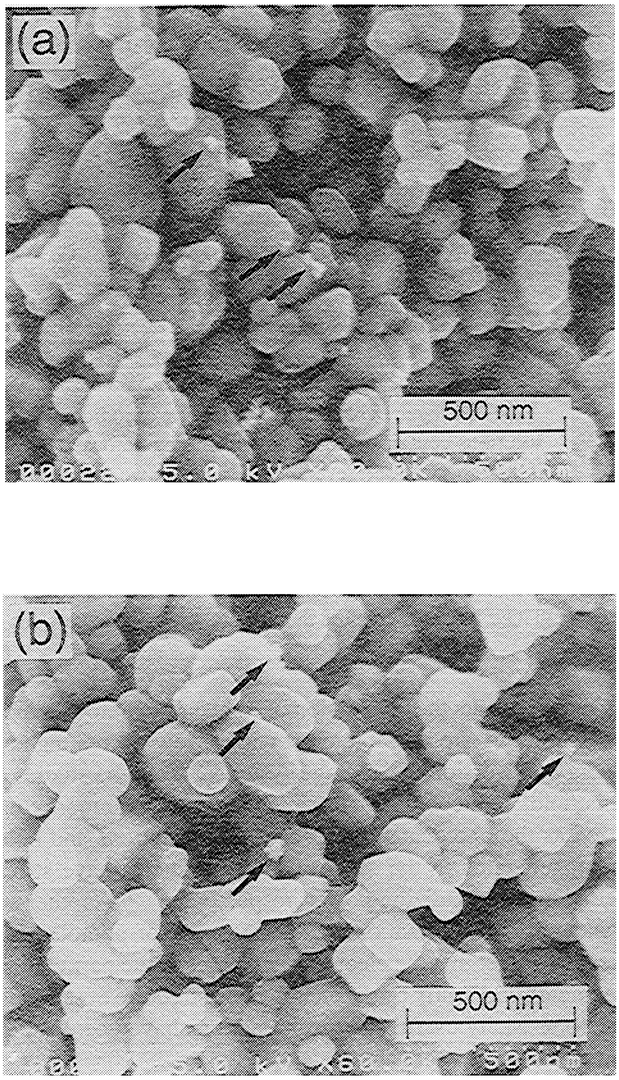

Fig. 1. SEM micrographs of TiO_2 powder (Kanto Chemical) loaded with 2 wt% Pt particles by mixing TiO_2 powder with Pt powder in an agate mortar (a), and of that after heat-treatment at 500 °C for 1 h (b). Some of the Pt particles are indicated by arrows.

Commercial platinum black powders contain platinum oxides to some extent. When the TiO_2 photocatalysts, on which such platinum black powder was loaded, were photoirradiated in the iodide containing solutions, the concentration of

PtI_6^{2-} ions in the solutions increased as the photoirradiation continued. Dabestani et al. reported that brominated platinum compounds ($PtBr_6^{2-}$) were generated by the photoirradiation of Pt-loaded TiO_2 particles in the presence of bromide ions.[30] In order to prevent such a reaction, we treated the photocatalysts with hydrogen before the photoirradiation in the manner described in the Experimental section. Because we used thus treated photocatalysts, PtI_6^{2-} ions were not generated even after prolonged irradiation of the photocatalysts.

In order to achieve the hydrogen evolution on the Pt-loaded TiO_2 particles under photoirradiation, we have tested a wide variety of TiO_2 powders under different experimental conditions. In the course of the tests, we found that some of the powders did show some activity for the hydrogen evolution and oxidation of iodide ions. A typical results for the production of I_3^- ions is shown by the solid line in Fig. 2. In this experiment, Pt-loaded TiO_2 powder (Kanto Chemical) was used after the heat-treatment at 500 °C. The evolution of hydrogen was also confirmed by gas-chromatography. The agreement between their amounts was confirmed under the improved experimental conditions, as will be discussed later. The broken line in Fig. 2 shows the result obtained using the Pt-loaded TiO_2 powder (Kanto Chemical) without the heat-treatment. In this case, no iodine or hydrogen was generated.

The above results indicate that the following reactions take place on the effective Pt-loaded TiO_2 photocatalysts.

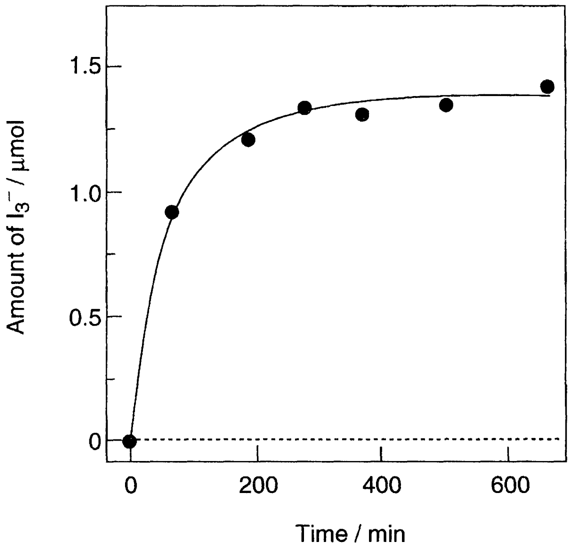

Fig. 2. Time-courses of the conversion of iodide ions into triiodide ions as the result of the photocatalytic reactions using the Pt-loaded TiO_2 (Kanto Chemical) particles. The solid and broken lines represent the results obtained on the photocatalysts with and without the heat-treatment at 500 °C for 1 h, respectively. The reaction was carried out in the cell containing the photocatalyst (200 mg) and 1.0 mol dm^{-3} aqueous solution of potassium iodide (50 ml) at pH 9.3.

$$h\nu(TiO_2) \rightarrow e^- + h^+ \quad (1)$$

$$e^- + h^+ \rightarrow \text{heat (recombination)} \quad (2)$$

$$e^- + H^+ \rightarrow 0.5\,H_2 \quad (3)$$

$$h^+ + I^- \rightarrow 0.5\,I_2 \text{ (or } I_3^-\text{)} \quad (4)$$

Since protons are weak electron acceptors, the reactions occurring in the cell are endothermic. Hence, the above result indicates that an endothermic and reversible reaction can be promoted on the semiconductor photocatalysts. This result is important from the viewpoint of energy conversion.

Even without the heat-treatment, the TiO_2 powder (Kanto Chemical) showed the activity when platinum was deposited photocatalytically from the aqueous solution of hydrogen hexachloroplatinate(IV). The activity of this photocatalyst was as high as that of the heat-treated photocatalyst, on which platinum was loaded by mixing in the agate mortar. These results suggest that the contact between platinum and TiO_2 particles is important to promote the reaction. We assume that the TiO_2 (Kanto Chemical) has an inactive layer on the surface, which is not observed by SEM. By the heat-treatment, the platinum is considered to migrate through the inactive layer and to make direct contact with the core part of the TiO_2 particles. On the other hand, the platinum particles photochemically deposited on TiO_2 are considered to be placed selectively on the sites having good electric contact with TiO_2, because by this method platinum is deposited electrochemically. Such photocatalysts are expected to show activity even without the heat-treatment, because of the deposition of platinum on the appropriate sites.

The presence of the inactive layer on the TiO_2 powder (Kanto Chemical) was evident from the fact that its activity was enhanced by washing with acids, especially with hydrofluoric acid. Such an effect by washing with acids was also observed for some other TiO_2 powders. SEM micrographs did not show the changes in the structure of the TiO_2 particles or in the distribution of the Pt fine particles deposited on them by the heat-treatment (Fig. 1) or by washing with acids. Hence, the improvement in the activity of the photocatalysts by these treatments is attributed to the improved contacts between Pt and TiO_2 but not to the amounts or the dispersion of the Pt particles deposited on the TiO_2 surface. Preliminary analysis of TiO_2 powder (Kanto Chemical) by XPS did not show the presence of any elements other than titanium and oxygen. The assignment of the inactive layer is underway.

The rates of the irreversible reactions, such as the oxidation of 2-propanol, on the Pt-loaded TiO_2 powder (Kanto Chemical) without the heat-treatment were much faster than that of the oxidation of iodide on the heat-treated powder by about 100 times when measured in the deaerated solutions of neutral pH. Interestingly, heat-treatment or washing of the photocatalysts did not give rise to the enhancement in the reaction rate for these irreversible reactions. These results suggest that there are severe conditions needed to promote the endothermic and reversible photocatalytic reactions.

Enhancement of the Reaction in the Acidic Solutions. The rate of the I_3^- generation and hydrogen evolution on the

Pt-loaded TiO_2 particles leveled off as the irradiation continued, as shown in Fig. 2. Such a behavior was observed for all the photocatalysts having photocatalytic activities for the oxidation of iodide and hydrogen evolution. The limitation of the concentration of I_3^- ions in solution at the stationary state is attributable to the back reactions of the products, as shown in Fig. 3. More precisely, as the concentration of the I_3^- ions in the solution increases, the rate of their reduction becomes comparable to and less than that of the reduction of protons. As a result, the reaction rate levels off. Another possible path of the back reaction is the oxidation of hydrogen by the holes generated in the TiO_2 particles. However, this possibility is neglected because very large amounts of hydrogen were obtained using alcohols as the electron donors.

Theoretically, the effect of the back reaction can be lessened by increasing the rate of the forward reaction. Figure 4 shows the initial reaction rate of the generation of iodine observed during the photoirradiation for 1 h in the solutions at different pH's using the heat-treated TiO_2 (Kanto Chemical). The results indicate that the reaction rate increases drastically by lowering pH.

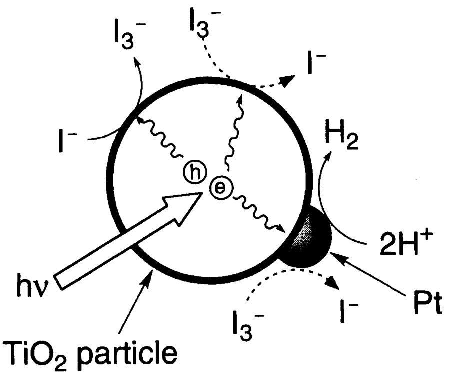

Fig. 3. Forward and back reactions which take place on a Pt-loaded TiO_2 particle under photoirradiation in the deaerated aqueous solution containing iodide ions.

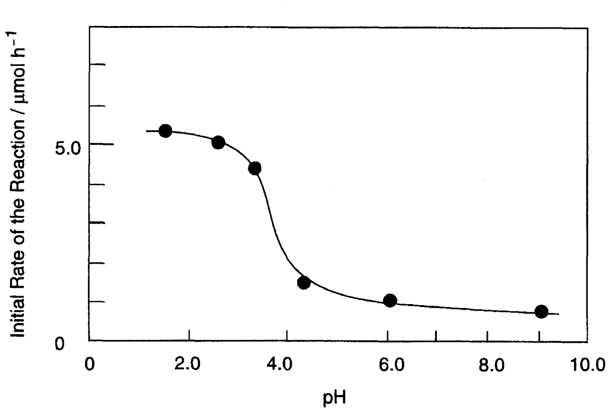

Fig. 4. pH dependence of the initial rate of the photocatalytic reaction using Pt-loaded TiO_2 (Kanto Chemical) particles as the photocatalyst. The reaction rates were determined from the amounts of triiodide ions generated during the photoirradiation for 1 h. The photocatalyst was heat-treated at 500 °C for 1 h.

We found that some kinds of TiO_2 powders, on which platinum black powder was loaded, had the activity for the hydrogen evolution from the solutions of iodide ions even without the heat-treatment. These powders are assumed not to have the inactive layer on the surface, because the washing with acids did not have any effect on their photocatalytic efficiency. The representative case is the TiO_2 powder (TIO-5). Figure 5 shows the time course of the evolution of I_3^- and hydrogen using the Pt-loaded TiO_2 (TIO-5) from the solution at pH 2.4. Under the conditions, the highest reaction rate has been obtained; the initial rate of hydrogen evolution and the limiting concentration of I_3^- ions are about 30 µmol h^{-1} and 15 µmol dm^{-3}, respectively. The agreement between the amounts of I_3^- and hydrogen generated is evidently seem in the figure. The relatively high initial reaction rate suggests that the present system has a chance to be applied to the energy conversion system, if a scheme for preventing the leveling-off of the reaction rate is successfully introduced. A possible method of such a scheme is the utilization of an electron relay across an oil/water boundary,[23] which would reduce the I_3^- ions to iodide ions.

The Mechanism of the Enhancement of the Reaction Rate under Acidic Conditions. In order to elucidate the reasons for the enhanced reaction rate in the solutions at low pH, the reactivity of iodide ions on the TiO_2 surface was measured using the TiO_2 film electrodes. The anodic current was observed in the presence of iodide ions at the electrode potentials more positive than 0.35 V vs. Ag/AgCl, which nearly agrees with the redox potential of I^-/I_3^-. This result indicates that iodide ions are electrochemically oxidized on the TiO_2 electrode. The anodic current density observed in the solutions of 2.0 mol dm^{-3} potassium iodide at 0.7 V vs. Ag/AgCl is plotted against the pH value in Fig. 6. At this potential the current density was negligibly small in the absence of iodide ions.

The anodic current on the TiO_2 electrodes was measured in the dark, in contrast to the reactions on the photocatalyst. Therefore, the oxidation of iodide ions in this electrochemi-

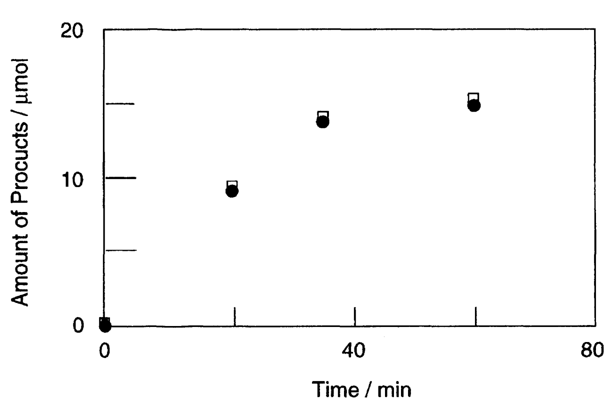

Fig. 5. Time-courses of the hydrogen evolution (□) and the conversion of iodide ions into triiodide ions (●) as the result of the photocatalytic reactions using the Pt-loaded TiO_2 (TIO-5) particles. The reaction was carried out in the cell containing the photocatalyst (200 mg) and 1.0 mol dm^{-3} aqueous solution of potassium iodide (50 ml) at pH 2.4.

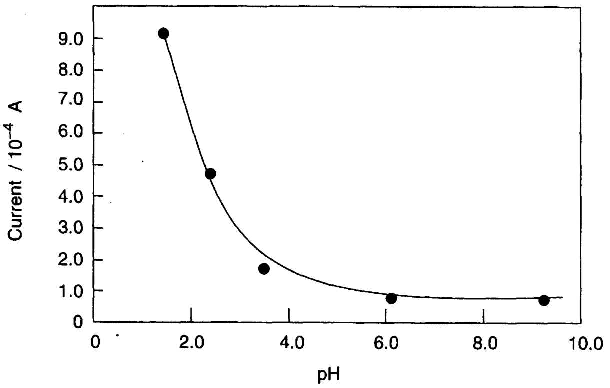

Fig. 6. pH dependence of the anodic current observed on the porous TiO_2 film electrode in the aqueous solution of 2.0 mol dm^{-3} potassium iodide at 0.7 V vs. Ag/AgCl.

cal measurement is not caused by the holes. The current is attributable to the tunneling of electrons through the space charge layer of the thin film TiO_2 electrode, as is often observed for the semiconductor electrodes having gap states at a high density. In such a case, the current is expected to reflect the amounts of the reactants adsorbed on the electrode surface. Hence, the similarity between the pH dependence of the photocatalytic oxidation of iodide (Fig. 4) and the anodic current (Fig. 6) suggests that the pH dependence is caused by the change of the adsorptivity of iodide ions on TiO_2.

The amounts of iodide ions adsorbed on the surface of TiO_2 powder were determined using an iodide-ion selective electrode. In the experiments, the decrease in the concentrations of the iodide ions in the solutions by the addition of TiO_2 powder was measured. The results indicate that the adsorptivity of iodide ions increases as the pH lowers, as shown in Fig. 7. The adsorptivity was not measured at pH's below 3.0 because of the limitation of the pH range of the ion-selective electrode.

The results obtained using the porous TiO_2 film electrodes and the iodide-ion selective electrode indicate that the pH dependence of the photocatalytic reaction is attributable to the change of the adsorptivity of iodide ions on TiO_2. The surface of the TiO_2 in aqueous solution is formally described by the following acid-base equilibria of the surface hydroxyl groups.[30]

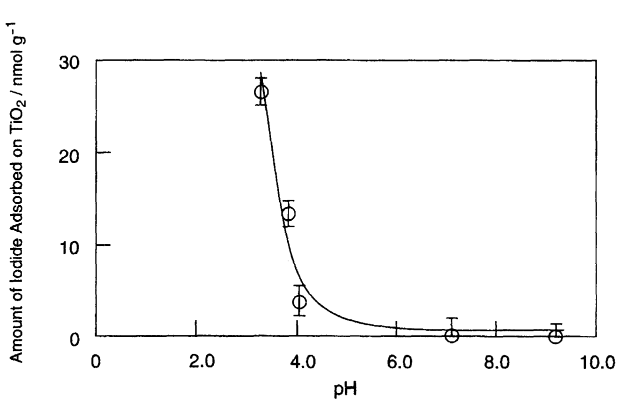

Fig. 7. pH dependence of the amount of iodide ions adsorbed on the TiO_2 (Kanto Chemical) powder. The adsorbed amounts were determined by measuring the concentration of iodide ions in solution using an iodide-ion selective electrode.

$$\equiv TiOH_2^+ \rightleftarrows \equiv TiOH + H^+ \quad pK_1$$
$$\equiv TiOH \rightleftarrows \equiv TiO^- + H^+ \quad pK_2$$

Using the equilibria the pH of zero point charge pH_{zpc} is given by

$$pH_{zpc} = (pK_1 + pK_2)/2.$$

Parks[32] and Moser and Grätzel et al.[33] reported that the values of pH_{zpc} for TiO_2 powder in aqueous phase range from 3.5 to 6.7. The reactivity and adsorptivity of iodide ions on TiO_2 powder increased steeply at pH's lower than 5, as shown by Figs. 4, 6, and 7. This correlation between the pH_{zpc} and the change of the reactivity suggests that the adsorption site of iodide ions on the surface of TiO_2 particles is the cationic species formed as the result of the acid-base equilibria.

Energetics of the Reaction. The standard Gibbs energy change for the formation of hydrogen and I_3^- from aqueous solution of iodide in the solution at pH 3 at room temperature is 137 kJ mol^{-1}. Hence, a part of the irradiated light energy is converted into chemical energy by the present photocatalyzed reaction system. However, the net reaction of the present system stops eventually as the products accumulate in the solution. The energy conversion can be attained by retarding the back process and by enhancing the forward process. For achieving the practical energy conversion, the reaction should be combined with other reaction systems, as the two photosystems are combined in the photosynthetic systems of green plants.[34]

Conclusion

We have demonstrated that endothermic and reversible reactions can be promoted on the Pt-loaded TiO_2 particles using iodide ions as the electron donor. Since the net reaction rate is determined by the competition between the forward and back processes, the control of these processes is of importance. The method of platinum loading on TiO_2 and the pH of solution are found to be useful for enhancing the forward process. These methods are useful, in combination with other reaction systems, for constructing new energy conversion and storage systems which mimick photosynthetic systems.

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References

1) A. Fujishima and K. Honda, *Nature*, **238**, 37 (1972).

2) Y. Nakato and H. Tsubomura, *Electrochim. Acta*, **37**, 897 (1992).

3) S. Claesson and B. Holmstrom "Solar Energy-Photochemical Processes Available for Energy Conversion," (Project Re-

sults: NE: 198214), National Swedish Board for Energy Source Development (1982).

4) G. T. Babcock, in "Photosynthesis," ed by J. Amesz, Elsevier, Amsterdam (1987), p. 125.

5) A. J. Bard, *Science*, **207**, 139 (1980).

6) A. J. Bard, *J. Electroanal. Chem.*, **168**, 5 (1984).

7) R. Memming, "Topics in Current Chemistry," Springer-Verlag, Berlin (1988), Vol. 143, p. 79.

8) S. R. Morrison, "Electrochemistry at Semiconductor and Oxidized Metal Electrodes," Plenum Press, New York (1980).

9) H. Gerischer, in "Physical Chemistry - An Advanced Treatise," ed by H. Eyring, D. Henderson, and W. Jost, Academic Press, New York (1970).

10) T. Kawai and T. Sakata, *J. Chem. Soc., Chem. Commun.*, **1980**, 694.

11) T. Kawai and T. Sakata, *Chem. Lett.*, **1981**, 81.

12) H. Ohnishi, M. Matsumura, H. Tsubomura, and M. Iwasaki, *Ind. Eng. Chem. Res.*, **28**, 719 (1989).

13) M. Matsumura, S. Furukawa, Y. Saho, and H. Tsubomura, *J. Phys. Chem.*, **81**, 1327 (1985).

14) S. Yanagida, H. Kawakami, Y. Midori, H. Kizumoto, C. Pac, and Y. Wada, *Bull. Chem. Soc. Jpn.*, **68**, 1811 (1995).

15) S. Kuwabata, R. Tsuda, and H. Yoneyama, *J. Am. Chem. Soc.*, **116**, 5437 (1994).

16) A. Fujishima, R. X. Cai, J. Otsuki, K. Hashimoto, K. Itoh, T. Yamashita, and Y. Kubota, *Electrochim. Acta*, **18**, 153 (1993).

17) T. Uchihara, M. Matsumura, A. Yamamoto, and H. Tsubomura, *J. Phys. Chem.*, **93**, 5870 (1989).

18) L. Spanhel, H. Weller, and A. Henglein, *J. Am. Chem. Soc.*, **109**, 6632 (1987).

19) K. R. Gopidas, M. Bohorquez, and P. V. Kamat, *J. Phys. Chem.*, **94**, 6435 (1990).

20) K. Yamaguchi and S. Sato, *J. Chem. Soc., Faraday Trans. 1*, **81**, 1237 (1985).

21) K. Domen, A. Kudo, T. Onishi, N. Kosugi, and H. Kuroda, *J. Phys. Chem.*, **90**, 292 (1986).

22) K. Sayama and H. Arakawa, *J. Phys. Chem.*, **97**, 531 (1993).

23) T. Ohno, K. Fujihara, S. Saito, and M. Matsumura, *Sol. Energy Mater. Sol. Cells*, in press.

24) M. Matsumura, T. Ohno, S. Saito, and M. Ochi, *Chem. Mater.*, in press.

25) K. Sayama and H. Arakawa, *J. Chem. Soc., Chem. Commun.*, **1992**, 253.

26) K. Sayama, A. Tanaka, K. Domen, K. Maruya, and T. Onishi, *J. Phys. Chem.*, **95**, 1345 (1991).

27) R. B. Draper and M. A. Fox, *Langmuir*, **6**, 1396 (1990).

28) C. Kormann, D. W. Bahnemann, and M. Hoffmann, *J. Phys. Chem.*, **92**, 5196 (1988).

29) B. O'Regan and M. Grätzel, *Nature*, **353**, 737 (1991).

30) R. Dabestani, X. Wang, A. J. Bard, A. Campion, M. A. Fox, S. E. Webber, and J. M. White, *J. Phys. Chem.*, **90**, 2729 (1986).

31) W. Stumm and J. J. Morgan, "Aquatic Chemistry," 2nd ed, Wiley Inrerscience, New York (1981), p. 625.

32) G. A. Parks, *Chem. Rev.*, **65**, 177 (1965).

33) J. Moser and M. Grätzel, *J. Am. Chem. Soc.*, **104**, 2977 (1982).

34) J. Darnell, H. Lodish, and D. Boltimore, "Molecular Cell Biology," 2nd ed, Scientific American Books, Inc., (1990).