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Photocatalytic production of hydrogen from water using TiO_2 and B/TiO_2

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Abstract

Photocatalytic decomposition of water has been studied by using TiO_2 (P25) and B/TiO_2 photocatalysts. Yield of the photocatalytic decomposition of water by TiO_2 (P25) depended on direction of light irradiation. The photocatalytic activity was about 10^3 times as high when the reaction cell was irradiated from the top as from the bottom. Modification of TiO_2 with boron oxides was found to be very effective for photocatalytic decomposition of water. TiO_2 modified with boron oxides exhibited high reactivity for the decomposition of water indifferently to the direction of light irradiation. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalytic decomposition of water; Direction of light irradiation; B/TiO_2

1. Introduction

For electrolysis of water, a potential difference of more than 1.23 eV is necessary between cathodic and anodic electrodes (Reaction 1), where the following anodic and cathodic reactions take place simultaneously (Reactions 2 and 3).

$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2, \quad E = 1.23\,\text{eV} \qquad (1)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-, \quad E^0(\text{pH}\,7) = -0.41\,\text{V vs. NHE} \qquad (2)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-, \quad E^0(\text{pH}\,7) = +0.82\,\text{V vs. NHE} \qquad (3)$$

This potential difference is equivalent to the energy of a wavelength of approximately 1008 nm. Therefore, if the energy of light is used effectively in an electrochemical system, it should be possible to decompose water with visible light of wavelength shorter than 1008 nm.

Although water splitting by solar light irradiation has been investigated by many researchers, any useful and applicable method has not been developed yet. Because water is transparent to visible light, it cannot be decomposed by visible light alone. It can be decomposed by irradiation alone only with ultraviolet light shorter than 190 nm. Honda and Fujishima [1,2] were the first to study photodecomposition of water over semiconductor photoelectrolysis cells using light of wavelength $\lambda<400$ nm. From Honda and Fujishima's results, it was suggested that water could be decomposed by light into oxygen and hydrogen according to the following schemes:

$$TiO_2 + 2h\nu \rightarrow 2e^- + 2h^+ \quad \text{(excitation of } TiO_2 \text{ by UV light)}$$

$$2h^+ + H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^+ \quad \text{(at the } TiO_2 \text{ electrode)}$$

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$2e^- + 2H^+ \rightarrow H_2$ (at the Pt electrode)

The overall reaction can be expressed as: $H_2O + 2h\nu \rightarrow \frac{1}{2}O_2 + H_2$.

Despite the success of Honda–Fujishima, use of a photoelectrochemical cell involves the difficulty of constructing the oxide semiconductor photoelectrode. Therefore, applications of the principle of water photodecomposition using semiconductor to heterogeneous photocatalytic systems using powdered semiconductors instead of photoelectrodes have been actively studied by reason of their advantages over photoelctrochemical cells, i.e., low cost to construct, chemical stability under the light, and large surface area. Such attempts have been supported by two experimental advances. One is accumulation of data on photocatalytic reactions over powdered semiconductors [3–16], while the other is Bard's concept that can be pictured as a "short-circuited" photoelectrochemical cell where semiconductor electrode and metal counter electrode have been brought into contact in single particle [17–20].

TiO_2 has been most widely used for studies of photocatalytic decomposition of water, because of its high stability against photocorrosion and its favorable band-gap energy. Most of the studies [21–24] concluded, however, that in aqueous suspension systems Pt–TiO_2 could not decompose water stoichiometrically, and the photocatalytic activities dropped rapidly with reaction time. On the other hand, high activities in the photocatalytic decomposition of water were often obtained by addition of so-called "sacrificial reagents" [25–29]. This suggests that photoexcited electrons and holes can be efficiently separated in a small semiconductor particle and that they are available for an irreversible chemical reaction, oxidization of sacrificial reagent. It is, therefore, inferred that a low efficiency of photodecomposition of water into H_2 and O_2 is mainly due to a rapid reverse reaction between produced H_2 and O_2. Thus, a critical problem to be resolved for realizing the up-hill reaction efficiently is how to prevent such thermodynamically favored reverse reaction.

In the present work, we clarified that the direction of light irradiation to the reaction cell is an important factor for suppression the reverse reaction in aqueous suspension of Pt-loaded TiO_2 photocatalyst. We also studied influence of modification of the photocatalyst with boron oxides on the photocatalytic activity for decomposition of water.

2. Experimental

2.1. Photocatalysts

TiO_2 powder obtained from Degussa (P25, anatase 78%) was used as the photocatalyst without any pre-treatment. H_2PtCl_6 (Pt 0.1 wt.% per P25) was loaded on the P25 powder using the photochemical deposition method.

B/TiO_2 catalyst was prepared by the sol–gel method using 2,4-pentanedione (PTN) as an organic ligand under an argon atmosphere. Titanium (IV) ethoxide (25.0 g) and boric acid triethyl ester (16.0 g) were dissolved in ethanol (12.6 ml). When 2,4-pentanedione (21.9 g) was added to the mixed solution, the color of solution turned to deep yellow. Then, H_2O (7.9 g) was added to the yellow solution. By keeping the solution at room temperature for 2 weeks, deep yellow B/Ti gel was obtained. The B/Ti gel was crushed and then calcined in O_2 at a specified temperature. H_2PtCl_6 (Pt 0.1 wt.% per B/TiO_2 photocatalyst) was loaded on the B/Ti powders using the impregnation method. Platinized B/Ti powders were reduced by H_2 at 473 K.

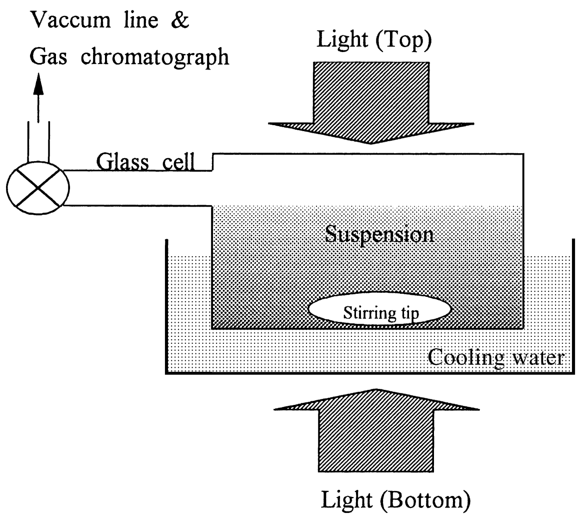
B_2O_3 powder was obtained from Kishida chemicals.

2.2. Characterization

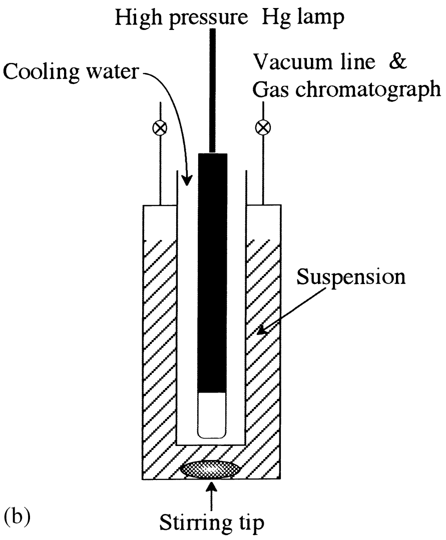
X-ray diffraction patterns of the B/Ti photocatalysts were obtained with a Rigaku RINT-2000 diffractometer using Cu Kα radiation. Surface area was measured with a Shimadzu FlowSorb-II 2300. UV–vis reflectance spectra were measured at 295 K with an Otsuka MCPD-1000 and normalized with a PC-98 computer. DTA curves were recorded using an Ulvac TGD-9600. The photographs of scanning electron microscope and transmission electron microscope were obtained with a Hitachi S-5000 and a HF-2000 FE, respectively.

2.3. Photocatalysis

The photocatalytic decomposition of water was performed at 295 K using an external-irradiation system (Fig. 1a) or an inner-irradiation system (Fig. 1b). The light source used in the external-irradiation system was a 250 W high pressure Hg lamp (Usio, Spot Cure). Photon flux was about 1.8×10^{18} photons/s when Toshiba UV-D35 filter was used. The inner-irradiation system is equipped with a 400 W high pressure Hg lamp (Riko, UVL-400P). After photocatalyst and water had been introduced to the reaction cell, the aggregated photocatalyst was suspended by magnetic stirring. The temperature of the reaction cell was controlled to 295 K with a water bath. The evolved gas was collected at defined reaction intervals and analyzed by gas chromatography (Ar carrier, MS5A column).



(a) External-irradiation system



(b)

Fig. 1. Apparatus for photocatalytic decomposition of water: (a) external-irradiation system; (b) inner-irradiation system.

3. Results and discussion

3.1. Effect of the direction of light irradiation

Fig. 2a shows the amount of evolved H_2 and O_2 over Pt-loaded TiO_2 as a function of time when the suspension was irradiated from the top of the reaction cell. Though the O_2 evolution is less than half the H_2 evolution (H_2/O_2=2.6 at 4 h), both H_2 and O_2 were evolved into the gas phase through all the runs. The shortage of O_2 at the first run can be attributed to the presence of residual organic compounds in the system, which act as sacrificial electron donors. After the second run, H_2 and O_2 were evolved stoichiometrically (H_2/O_2=2.0–2.1). Furthermore, the photocatalytic activities did not deteriorate even after 14 h of irradiation. The partial pressures of H_2 and O_2

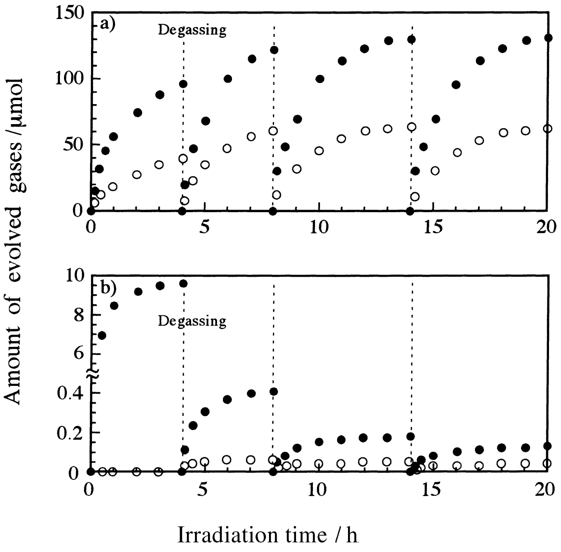


Fig. 2. Reaction profile of decomposition of water over the Pt-loaded photocatalyst: (a) irradiation from the top; (b) irradiation from the bottom. (●) H_2, (○) O_2 catalyst: 0.3 g, water: 16 ml, high pressure Hg lamp (250 W), external-irradiation system.

increased with the UV irradiation time, and then saturated when they reached 2.2 and 1.1 kPa, respectively. The average rate of H_2 evolution during the initial 5 min of the fourth run is 106 μmol/h without filter and 76 μmol/h with the filter (Toshiba, UVD-35), which means 1.4% of quantum efficiency.

Fig. 2b shows the evolved H_2 and O_2 amount over the Pt-loaded TiO_2 as a function of time when the suspension was irradiated from the bottom of the reaction cell. Although the yield was less than when irradiated from the top, H_2 was evolved into the gas-phase. However, as the reaction proceeded, the rate of H_2 evolution decreased rapidly. This decrease in the H_2 evolution rate could be attributed to consumption of residual organic compounds, which act as sacrificial electron donors. The average rate of H_2 evolution for the initial 5 min of the fourth run, shown in Fig. 2b, was 0.12 μmol/h: this is about 10^{-3} times of that with irradiation from the top. Though the evolution of O_2 can be observed from the second run, the rate did not reach the stoichiometric value. These results clearly indicate that the photocatalytic reactivity of Pt-loaded TiO_2 (P25) in the photocatalytic decomposition of water strongly depends on the direction of light irradiation.

What made the photocatalytic efficiency depend on the light direction? The distribution of light absorption in the suspension systems containing the semiconductor particles is shown in Fig. 3. A high pressure Hg lamp (250 W) was used as the UV light source. Transmittance of UV light drops gradually with the depth of the suspension system, and below 0.2 mm light could not penetrate. These results mean that in the case of irradiation from the bottom, light did not reach the upper suspension. Therefore, the loaded Pt particles on the photocatalysts in the upper suspension act only as reverse reaction sites, the photocatalysts apparently exhibiting low efficiency in the decomposition of water due to the fast reverse reaction on Pt sites.

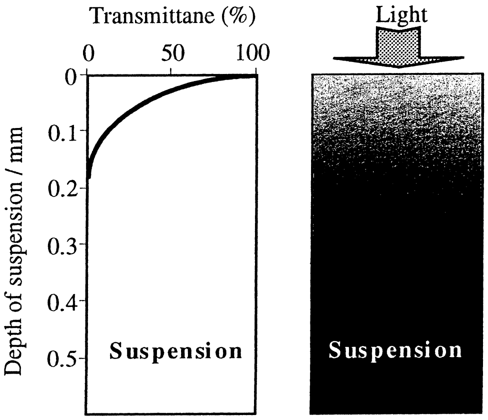


Fig. 3. Distribution of light absorption in the suspension systems containing the semiconductor particles.

3.2. Modification of the photocatalyst with boron oxides

A microstructural nature of the TiO_2 modified with boron (B/TiO_2) was examined by various techniques, such as SEM, TEM, and X-ray diffractograms. Fig. 4 shows the SEM and TEM micrographs of B/TiO_2 photocatalysts calcined at various temperatures. A clear relationship between the crystallinity of B/TiO_2 photocatalyst and calcination temperature was observed. The obtained B/Ti gel was amorphous before calcination (Fig. 4a and b). After calcination in oxygen, the formation of microcrystal was observed in the B/TiO_2 photocatalyst, and with increasing calcination temperature the microcrystal size of the B/TiO_2 photocatalyst gradually increased, accompanied by decrease in the surface area. Phase separation in the B/TiO_2 photocatalysts was not observed for all samples, indicating the B/TiO_2 photocatalysts having a homogeneous structure were prepared by the sol–gel method.

In order to obtain information on the crystal structure of the B/TiO_2 photocatalysts, X-ray diffraction patterns of the photocatalysts were measured. Fig. 5 shows the XRD patterns of the B/TiO_2 photocatalysts calcined at various temperatures. Fig. 5a is the XRD pattern of diboron trioxide as a reference. The XRD pattern of the B/TiO_2 photocatalyst calcined at 673 K shows diffraction lines attributed to the anatase phase of TiO_2 beside the peak due to the diboron trioxide, as shown in Fig. 5b. An increase in the calcination temperature caused the diffraction lines of the anatase phase to increase in intensity. A further increase in the calcination temperature beyond 973 K led to disappearance of the diffraction lines attributed to the anatase phase. The diffraction lines due to the rutile phase of TiO_2 appeared when calcined at 973 K and increased in intensity at 1173 K, where only the diffraction lines attributed to the rutile phase were ob-

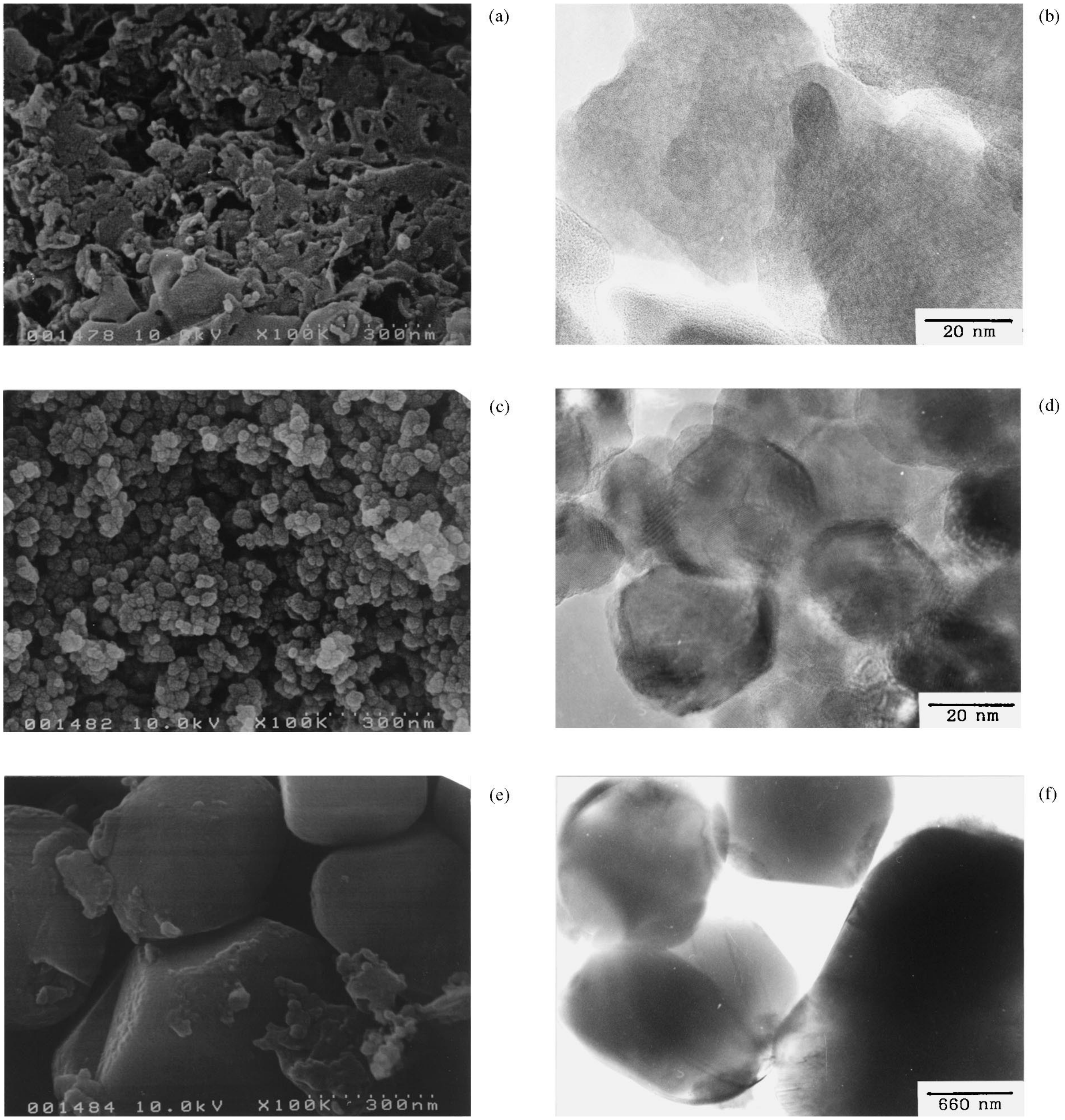


Fig. 4. SEM (a, c, e) and TEM (b, d, f) micrographs of B/TiO_2 photocatalysts calcined at various temperatures: (a, b) with no treatment; (c, d) calcined at 773 K; (e, f) calcined at 1173 K.

served. These results clearly show that an increase in the calcination temperatures transforms the crystalline structure of the titanium oxides from amorphous to anatase, and then to rutile.

Fig. 6 shows the normalized UV–vis reflectance spectra of the TiO_2 (P25) and B/TiO_2 photocatalysts. It is clear that with increasing calcination temperature the absorption band of the catalysts shifts remarkably

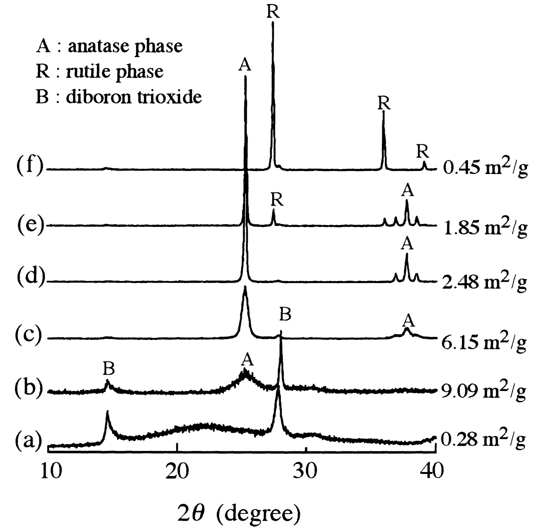


Fig. 5. X-ray diffraction patterns and surface area of B/TiO$_2$ photocatalysts: (a) powdered B$_2$O$_3$; (b) B/TiO$_2$ photocatalyst calcined at 673 K; (c) at 773 K; (d) at 873 K; (e) at 973 K; (f) at 1173 K.

towards longer wavelengths. It is well known that TiO$_2$ (P25) has two UV absorption bands due to anatase phase (387 nm) and rutile phase (413 nm). On the other hand, no UV absorption band in the 200–400 nm range was observed for the powdered B$_2$O$_3$. Therefore, such a large shift towards longer wavelengths observed for the B/TiO$_2$ photocatalysts indicates that the phase transition of titanium oxide species in the binary oxides from an anatase phase to a rutile phase occurs with the increase in the calcination temperature.

Fig. 7 shows the typical DTA curves of P25 and B/TiO$_2$ photocatalyst. A broad endothermic peak can be observed between 373 and 473 K. The peak is due to the dehydration of the binary oxide. It was also found that the intensity of this peak due to dehydration gradually increases with increase in the ratio of boron in the B/TiO$_2$ catalysts (data not shown). However, for the TiO$_2$ sample without any modification, the peak due to dehydration was not observed. These results clearly indicate that the modification of TiO$_2$ with boron oxides is able to enhance the ability for the hydration of the photocatalysts; such enhanced ability of hydration plays a significant role in achieving a high yield of the photocatalytic decomposition of water.

Titanium oxide photocatalysts modified with boron oxides exhibited high photocatalytic reactivity in the decomposition of water. Irradiation of UV light on the Pt-loaded B/TiO$_2$ photocatalyst in suspension led to the decomposition of water, and H$_2$ and O$_2$ were evolved. Fig. 8 shows the reaction time profiles of the evolution of H$_2$ and O$_2$ in the photocatalytic decomposition of water on the Pt-loaded B/TiO$_2$ photocatalyst calcined at 773 K. As shown in Fig. 8, the amount of evolved H$_2$ increased linearly with the UV irradiation time. H$_2$ and O$_2$ were evolved stoichiometrically

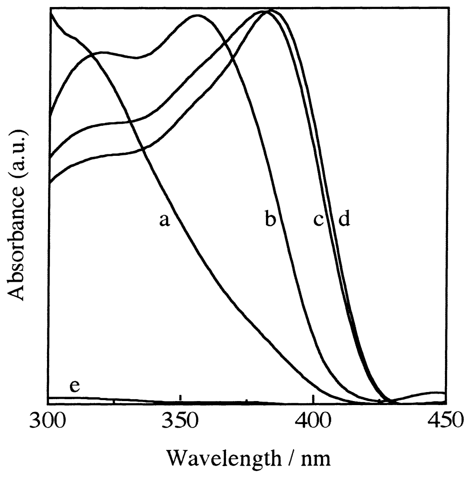


Fig. 6. UV–vis reflectance spectra of the B/TiO$_2$ photocatalyst: (a) P25; (b) B/TiO$_2$ photocatalyst calcined at 773 K; (c) at 973 K; (d) at 1173 K; (e) powdered B$_2$O$_3$.

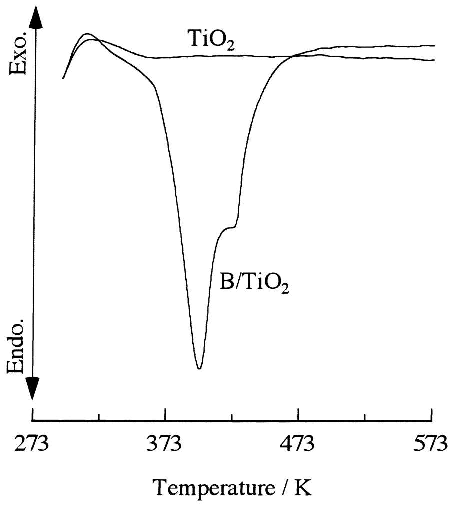


Fig. 7. Typical DTA curves of TiO$_2$ and B/TiO$_2$ photocatalyst.

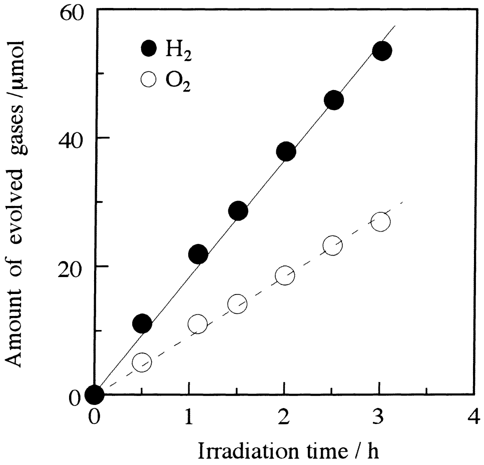


Fig. 8. Reaction profile of the decomposition of water over the Pt-loaded B/TiO_2 photocatalyst calcined at 773 K. Catalyst: 0.3 g, water: 350 ml, high pressure Hg lamp (400 W), inner-irradiation system.

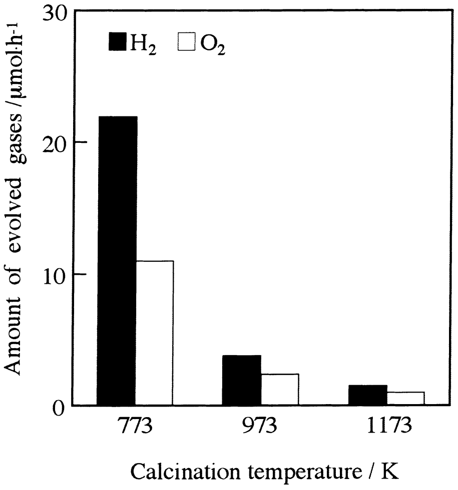


Fig. 9. Effect of calcination temperature of B/TiO_2 photocatalyst on photocatalytic activity for decomposition of water. Catalyst: 0.3 g, water: 350 ml, high pressure Hg lamp (400 W), inner-irradiation system.

(H_2/O_2=2.0) through the reaction run. Furthermore, the photocatalytic reactivity did not deteriorate until 12 h after the run. However, with the irradiation time, the photocatalytic reactivity gradually deteriorated after 12 h of the run since the rate of the reverse reaction increased with increasing concentrations of H_2 and O_2 in the gas phase. The average rate (three runs) of H_2 evolution for the B/TiO_2 photocatalyst calcined at 773 K was determined to be 21.9 µmol/h.

The effect of the calcination temperature on the photocatalytic activities was also studied. Fig. 9 shows the dependence of the photocatalytic activities on the calcination temperature. H_2 and O_2 evolution under UV irradiation decreased with the increasing calcination temperature. The stoichiometric evolution of O_2 was observed only for the photocatalyst calcined at 773 K. These results indicate that the Pt-loaded B/TiO_2 photocatalysts decompose water stoichiometrically in aqueous suspension system under irradiation with UV light, and the photoactivity of Pt-loaded B/TiO_2 photocatalyst for decomposition of water strongly depends on the crystal structure of titanium oxide species in the B/TiO_2 catalyst.

Another role of boron oxides for achieving a high yield in the photocatalytic decomposition of water is suppressing recombination of the evolved H_2 and O_2. As has been mentioned, in Pt-loaded TiO_2 aqueous suspension systems, the photocatalytic reactivity for the decomposition of water changed depending on the direction of light irradiation, and that stoichiometric water decomposition could only be observed when the suspension systems were irradiated from the top of the reaction cell. In the inner irradiation system, Pt-loaded TiO_2 did not exhibit any apparent reactivity for the decomposition of water because of the fast reverse reaction of the H_2 and O_2. However, in the same inner irradiation system, the Pt-loaded B/TiO_2 photocatalysts decomposed water into H_2 and O_2. Thus, the stoichiometric decomposition of water was found to proceed on the Pt-loaded B/TiO_2 photocatalysts in suspension systems without any changes in the yields of H_2 and O_2 caused by the direction of UV light irradiation, i.e., external-irradiation, or inner-irradiation. Such striking contrast between the Pt-loaded TiO_2 photocatalyst and the Pt-loaded B/TiO_2 photocatalyst clearly indicates that the boron oxides in the B/TiO_2 photocatalyst play a significant role in the suppression of the recombination of the evolved H_2 and O_2 in the reaction system.

4. Conclusions

The change in the direction of light was found to lead to the significant differences for the yield of the photocatalytic decomposition of water. The photocatalytic activity was about 10^3 times as high when the reaction cell was irradiated from the top as from the bottom. Stoichiometric evolution of H_2 and O_2 was observed only for the irradiation from top of the reaction cell.

TiO_2 photocatalysts modified with boron oxides decomposed water stoichiometrically in aqueous suspension systems. Their photocatalytic activities were strongly dependent on the crystal phase of the titanium oxide in the B/TiO_2 photocatalyst. It was also found that the photocatalytic activity of the Pt-loaded B/TiO_2 photocatalysts for the decomposition of water in suspension systems was not affected by the changes in the direction of light irradiation, i.e., external-irradiation or inner-irradiation.

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References

[1] A. Fujishima, K. Honda, Bull. Chem. Soc. Jpn. 44 (1971) 1148.
[2] A. Fujishima, K. Honda, Nature 238 (1972) 37.
[3] E. Bauer, C. Neuweiler, Helv. Chim. Acta 10 (1927) 901.
[4] V.I. Veselovskii, D.M. Shub, Zh. Fiz. Khim. 26 (1952) 509.
[5] T.R. Rubin, J.G. Calvert, G.T. Rankin, W.M. MacNevin, J. Am. Chem. Soc. 75 (1953) 2850.
[6] M.C. Markham, K.J. Laidler, J. Phys. Chem. 57 (1953) 363.
[7] G.M. Schwab, Adv. Catal. 9 (1953) 229.
[8] J.G. Cavert, J. Theurer, G.T. Rankin, W.M. MacNevin, J. Am. Chem. Soc. 76 (1954) 2575.
[9] G.A. Korunovskii, Yu.S. Lebedev, Zh. Fiz. Khim. 35 (1961) 1078.
[10] J.C. Kuriacose, M.C. Markham, J. Phys. Chem. 65 (1961) 2232.
[11] S. McLintock, M. Ritchie, Trans. Faraday Soc. 61 (1965) 1007.
[12] M. Yamamoto, G. Oster, J. Polym. Sci. 4 (1966) 1683.
[13] R.C. Oppenheim, A.S. Buchanan, T.W. Healy, Aust. J. Chem. 20 (1967) 1743.
[14] S.R. Morrison, T. Freund, J. Chem. Phys. 47 (1967) 1543.
[15] H. Gerischer, Surf. Sci. 18 (1969) 97.
[16] T. Freund, W.P. Gomes, Catal. Rev. 3 (1970) 1.
[17] B. Kraeutler, A.J. Bard, J. Am. Chem. Soc. 100 (1978) 4317.
[18] A.J. Bard, J. Photochem. 10 (1979) 59.
[19] A.J. Bard, Science 207 (1980) 139.
[20] A.J. Bard, J. Phys. Chem. 86 (1982) 172.
[21] D. Duonghong, E. Borgarello, M. Gratzel, J. Am. Chem. Soc. 103 (1981) 4685.
[22] A. Mils, G. Porter, J. Chem. Soc., Faraday Trans. I 78 (1982) 3659.
[23] R.S. Magliozzo, A.I. Krasna, Photochem. Photobiol. 38 (1983) 15.
[24] G. Munuera, A.R. Gonzalez-Elipe, A. Fernandez, P. Malet, J.P. Espinos, J. Chem. Soc., Faraday Trans. I 85 (1989) 1279.
[25] H. Gerischer, in: B.O. Seraphin (Ed.), Solar Energy Conversion Topics in Applied Physics, Vol. 31, Springer, Berlin, 1979.
[26] H. Tributsch, Nature 281 (1979) 555.
[27] T. Kawai, T. Sakata, Nature 282 (1979) 283.
[28] T. Kawai, T. Sakata, Chem. Phys. Lett. 72 (1979) 87.
[29] T. Kawai, T. Sakata, Nature 286 (1980) 474.