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Characterization of titanium-boron binary oxides and their photocatalytic activity for stoichiometric decomposition of water

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Abstract

A titanium-boron binary oxide has been prepared by sol-gel method and used as a photocatalyst for the decomposition of water. The structure of titanium oxide species in the Ti/B binary oxide was amorphous before and crystal after calcination in O_2 , while the boron oxide species maintained its amorphous state. With increasing calcination temperature, the crystalline structure of titanium oxides changed from an anatase phase to a rutile phase. Pt-loaded Ti/B photocatalysts decomposed water stoichiometrically in aqueous suspension system. Their photocatalytic activity decreased markedly with increase in the calcination temperature, indicating that the photocatalytic activity of the Ti/B binary oxide was strongly dependent on the crystal phase of the titanium oxide in the Ti/B binary oxide. A remarkable yield in the reaction of water decomposition was obtained when Na_2CO_3 was added in the Pt-loaded Ti/B binary oxide suspension. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalyst; Water decomposition; Titanium-boron binary oxide

1. Introduction

Recently, the application of a principle of water decomposition over the photoelectrochemical cells to heterogeneous photocatalysis system using powdered semiconductors has been actively studied. TiO_2 has been mostly used as a powdered photocatalyst for the decomposition of water by reason of its high stability and favorable band-gap energy. However, most of the studies using the TiO_2 as a photocatalyst concluded that in aqueous suspension system Pt-loaded TiO_2 could not decompose water stoichiometrically, and the photocatalytic activities dropped rapidly with

the reaction time [1–4]. This inactivity of $Pt-TiO_2$ is caused by the efficient recombination of evolved hydrogen and oxygen in suspension. Tabata et al. have reported that the Pt-loaded TiO_2 decomposed water stoichiometrically in aqueous suspension system when the suspension was irradiated from the top [5]. On the other hand, according to the reports by Sayama et al. [6–9], addition of carbonates in the $Pt-TiO_2$ aqueous suspension system led to the stoichiometric water decomposition. However, until now there have been no reports on the photocatalysts capable of decomposing pure water stoichiometrically in aqueous suspension system free from the conditions mentioned above.

It is well known that binary oxide catalysts often exhibit higher catalytic activity than what one can

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predict from the properties of their components. Domen et al. have reported a successful stoichiometric decomposition of water over NiO loaded SrTiO_3 semiconductor in water vapor system [10,11]. Anpo et al. have also reported that a titanium-silicon binary oxide was highly active as a photocatalyst in photocatalytic reactions of alkenes and alkynes with water [12]. These results suggest that binary oxides are potentially useful photocatalysts. Therefore, we found it worthwhile to develop novel binary oxide catalysts to investigate their photocatalytic activity for the stoichiometric decomposition of water.

In the present work, we deal with the characterization of titanium-boron binary oxides by means of SEM, TEM, UV–VIS and XRD spectroscopic techniques and their photocatalytic activity for the decomposition of water using a closed gas-circulating system.

2. Experimental

The used Ti/B 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 solution turned deep yellow. Then H_2O (7.9 g) was added deliberately to the yellow solution. By keeping the solution at room temperature for two weeks, Ti/B gel having deep yellow color was obtained. The Ti/B oxide gel was crushed and then calcined in O_2 at a specified temperature in the region of 673–1173 K. TiO_2 was obtained from Degussa (P25, anatase 78%). B_2O_3 powder was obtained from Kishida chemicals. Platinum was loaded on the Ti/B powders using the impregnation method. The Ti/B binary oxide (1.0 g) was suspended in 100 ml of aqueous solution of H_2PtCl_6 (Pt 0.1 wt.% per Ti/B). After vacuum distillation, the residue was dried for one night and then calcined in H_2 at 473 K for 2 h.

X-ray diffraction patterns of the Ti/B binary oxide were obtained with a Rigaku RINT-2000 diffractometer using Cu K_α radiation. UV–VIS reflectance spectra were measured at 295 K by a Otsuka MCPD-1000 and normalized with a PC-98 computer. The micrographs of scanning electron microscope and

transmission electron microscope were measured by a Hitachi S-5000 and a HF-2000 FE at room temperature.

The photocatalytic decomposition of water was performed at 295 K using a closed gas-circulating system including an inner irradiation quartz cell (69 mm diameter, 230 mm height, 495 cm^3 volume) equipped with a 400 W high-pressure Hg lamp (Riko, UVL-400P). After 300 mg of Pt-loaded Ti/B binary oxide and 350 ml of water had been introduced to the reaction cell, the aggregated photocatalyst was suspended by magnetic stirring. Ar gas (40 kPa) was introduced when the suspension was well deaerated. 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).

3. Results and discussion

A microstructural nature of the Ti/B binary oxide was confirmed by various techniques, such as SEM, TEM, and X-ray diffractograms. Fig. 1 shows the SEM and TEM micrographs of Ti/B binary oxides calcined at various temperatures. A clear relationship between the crystallinity of Ti/B binary oxide and calcination temperature was observed. The obtained Ti/B gel was amorphous before calcination (Fig. 1(A,B)). After calcination in oxygen, the formation of microcrystal was observed in the Ti/B binary oxide, and with increasing the calcination temperature the microcrystal size of the Ti/B binary oxide was gradually increased to accompanied by the decrease in the surface area. Phase separation in the Ti/B binary oxides was not observed for all samples, indicating the Ti/B binary oxide having a homogeneous structure were prepared by the sol–gel method.

In order to obtain information on the crystal structure of the Ti/B binary oxides, X-ray diffraction patterns of the photocatalysts were investigated. Fig. 2 shows the XRD patterns of the Ti/B binary oxide calcined at various temperatures. Fig. 2(a) is the XRD pattern of diboron trioxide. As shown in Fig. 2(b) the XRD pattern of the Ti/B binary oxide calcined at 673 K shows the diffraction line attributed to an anatase phase of titanium oxide beside the peak due to boron trioxide. With calcination temperature,

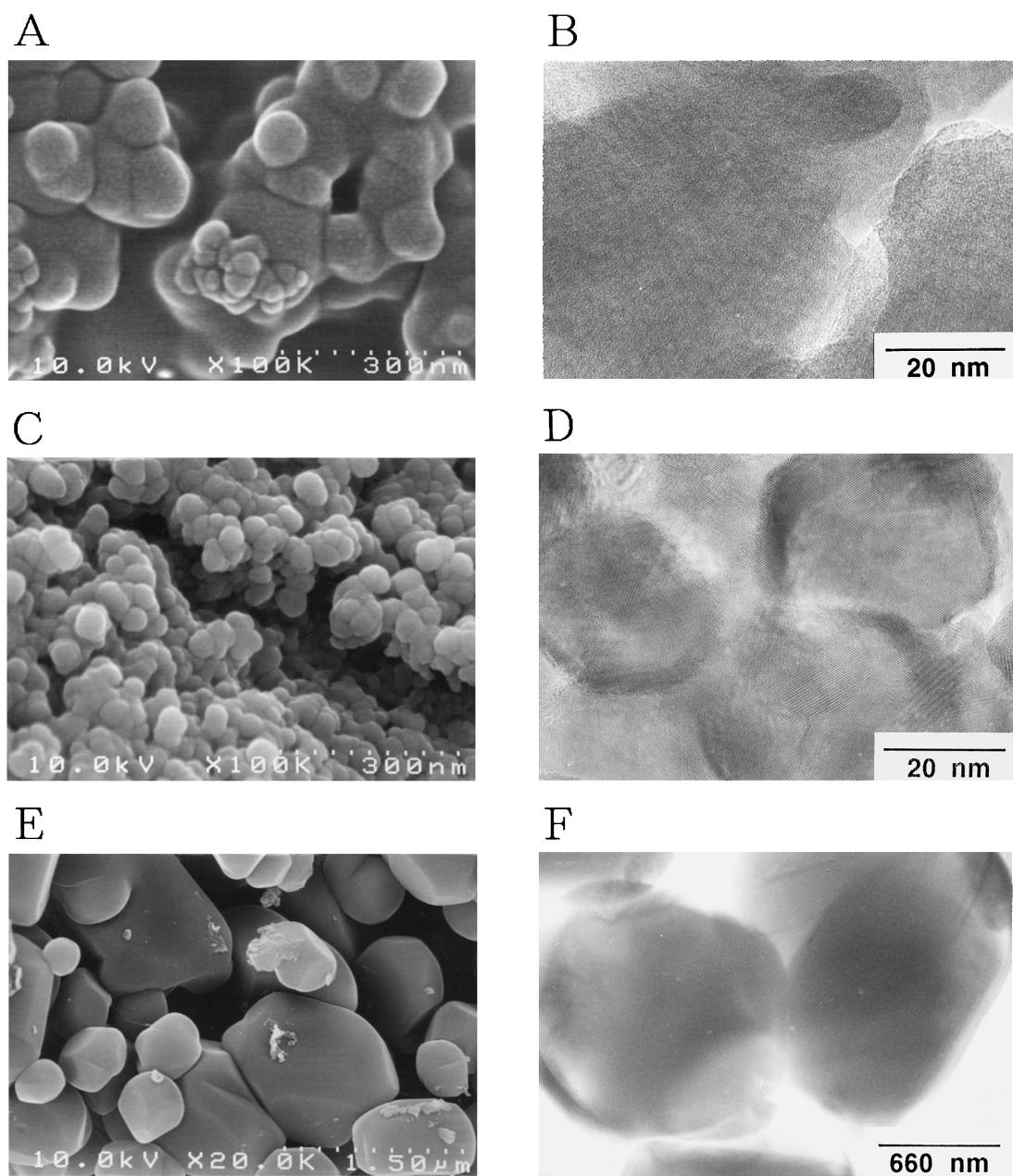


Fig. 1. SEM (A, C, E) and TEM (B, D, F) micrographs of the Ti/B binary oxides calcined at various temperatures; A,B: with no treatment, C,D: calcined at 773 K, E,F: calcined at 1173 K.

the diffraction lines due to the anatase phase increased in intensity. A further increase in the calcination temperature beyond 973 K led to disappearance of the X-ray diffraction lines attributed to the anatase phase of TiO_2 . The diffraction lines due to a rutile

phase of TiO_2 appeared at 973 K and increased in intensity at 1173 K. At 1173 K, only the diffraction lines attributed to the rutile phase were observed. Together with the microscopic analysis, these results indicate that with increase in calcination temperature,

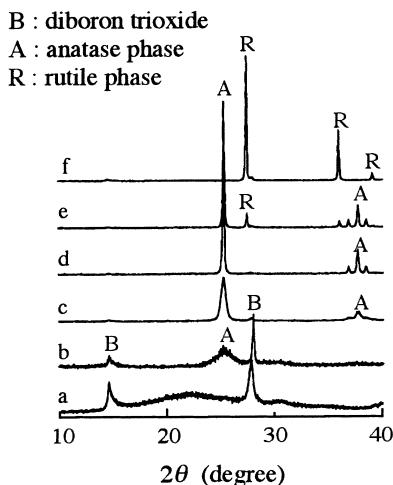


Fig. 2. X-ray diffraction patterns of B_2O_3 powder and the Ti/B binary oxides; (a) powdered B_2O_3 , (b) Ti/B binary oxide calcined at 673 K, (c) at 773 K, (d) at 873 K, (e) at 973 K, (f) at 1173 K.

the crystalline structure of titanium oxides changes from amorphous state to an anatase phase, and then to a rutile phase in B_2O_3 matrices.

Fig. 3 shows the normalized UV–VIS reflectance spectra of the TiO_2 (P25) and the Ti/B binary oxides. It is clear that with increasing calcination temperatures the absorption band of the binary oxides shifts remarkably 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–

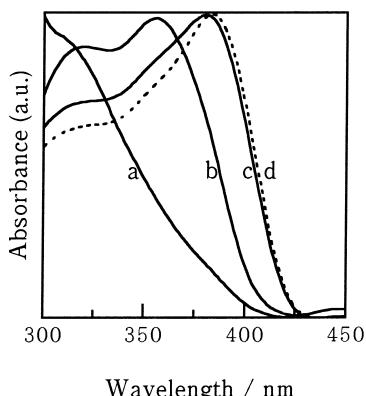


Fig. 3. UV-vis reflectance spectra of the Ti/B binary oxides; (a) powdered TiO_2 (P25), (b) Ti/B binary oxide calcined at 773 K, (c) at 973 K, (d) at 1173 K.

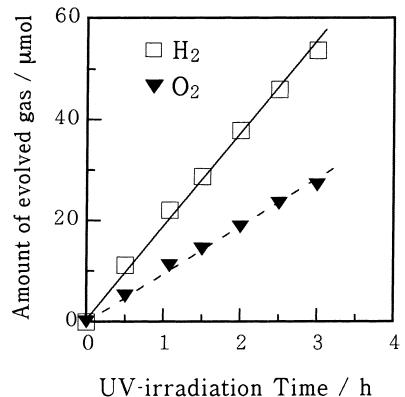


Fig. 4. The reaction profile of the decomposition of pure water over the Pt-Ti/B binary oxide under UV-irradiation.

400 nm range was observed for the powdered B_2O_3 . Therefore, it can be said that such a large shift towards longer wavelengths observed with the Ti/B oxides indicates the phase transition of titanium oxide species in the binary oxides from an anatase phase to a rutile phase with the increase in the calcination temperature.

The irradiation of UV light on a Pt-loaded Ti/B binary oxide in aqueous suspension led to the decomposition of water to evolve H_2 and O_2 . Fig. 4 shows time course of the evolution of H_2 and O_2 by the photocatalytic decomposition of water. The Ti/B binary oxide calcined at 773 K was used as a photocatalyst. As shown in Fig. 4, the amount of evolved H_2 increased linearly with the UV-irradiation time. H_2 and O_2 were evolved stoichiometrically ($\text{H}_2/\text{O}_2=2.0$) through the reaction run. Furthermore, the photocatalytic activity did not deteriorate until the 12 h of the run. However, with the irradiation time, the photocatalytic activity deteriorated gradually after the 12 h of the run because the rate of the reverse reaction increased with H_2 and O_2 concentrations in the gas phase. The average rate (three runs) of H_2 evolution for the Ti/B photocatalyst calcined at 773 K was $21.9 \mu\text{mol h}^{-1}$.

The effect of the calcination temperature on the photocatalytic activity was also studied. Table 1 shows the dependence of the photocatalytic activities on the calcination temperature. The activities of H_2 and O_2 evolution under UV-irradiation was remarkably decreased with increasing calcination temperature. The stoichiometric evolution of O_2 was observed

Table 1
The rates of H_2 and O_2 evolution over the Pt-loaded Ti/B binary oxide in aqueous suspension systems

Calcination temperature	Na_2CO_3 mol	Rate of evolved gas ($\mu\text{mol h}^{-1}$)		Ratio of H_2/O_2
		H_2	O_2	
773 K	None	21.9	11.0	1.99
873 K	None	11.0	5.6	1.96
973 K	None	3.8	2.4	1.58
1173 K	None	1.5	1.0	1.50
	None	11.0	5.6	1.96
	0.266	234	117	2.00
873 K	0.532	915	458	2.00
	0.798	1872	936	2.00
	0.931	2156	1078	2.00

Inner-irradiation system, catalyst: 0.3 g, water: 350 ml, Hg lamp: 400 W.

only for the Ti/B binary oxide calcined at 773 K, and the ratio of H_2/O_2 deviated gradually with the calcination temperature. These results indicate that the Pt-loaded Ti/B photocatalysts decompose water stoichiometrically in aqueous suspension system under irradiation of UV light, and the photoactivity of Pt-Ti/B binary oxide for decomposition of water strongly depends on the crystal structure of titanium oxide species in the Ti/B binary oxide.

Table 1 also shows the initial activity of H_2 and O_2 evolution under UV-irradiation when Na_2CO_3 was added to the Pt-loaded Ti/B binary oxide suspension. Sayama et al. have reported that an addition of carbonate salts to Pt-loaded TiO_2 suspensions led to highly efficient stoichiometric photocatalytic decomposition of liquid water into H_2 and O_2 , and the H_2 and O_2 evolution rates strongly depended on the concentration of the carbonate salts [6–9]. The role of carbonate salts, at present time, is not clear, but the remarkable increase of evolution rate is worthy of note. We, therefore, investigated the effect of the carbonate on the rates of H_2 and O_2 evolution in the Pt-Ti/B aqueous suspension system. It was found that the rates of H_2 and O_2 evolution rapidly increased with Na_2CO_3 addition. The rate of increase strongly depended on the Na_2CO_3 concentration, and the maximum rate of gas evolution was obtained in the case of 0.931 mol Na_2CO_3 addition to the Ti/B aqueous suspension system. It was also found that H_2 and O_2

evolved stoichiometrically ($H_2/O_2=2.0$) for all reaction runs when Na_2CO_3 was added in the suspension.

Tabata et al. have reported that in Pt-TiO₂ aqueous suspension system the photocatalytic activity for the water decomposition was different depending on the irradiation direction, and the stoichiometric water decomposition was observed when the suspension was irradiated from the top [5]. Their Pt-TiO₂ could not decompose water in the reaction system used in the present work, i.e., the inner irradiation system. It can be seen, therefore, that in the inner irradiation system the Pt-TiO₂ which can intrinsically decompose pure water stoichiometrically do not apparently exhibit the photocatalytic activity by reason of the fast reverse reaction of the evolved H_2 and O_2 into water. We have also investigated the water decomposition over the Pt-Ti/B photocatalyst with the top-irradiated suspension system. The stoichiometric decomposition of water over the Pt-Ti/B binary oxide was observed also in the top-irradiated suspension system, although amounts of evolved gases were less than those of the Pt-TiO₂. Together with the results obtained by Tabata et al., it is concluded that the boron oxide in the Ti/B binary oxide contributes to the suppression of the recombination of the evolved H_2 and O_2 in suspension. At this moment, details of role of the boron oxide in the Ti/B binary oxide is not clear and is now under investigation.

4. Conclusions

Using the sol-gel technique, Ti-B binary oxide catalyst was prepared in a homogeneous structure. After calcination, the titanium oxide in the Ti/B binary oxides having an amorphous state was crystallized in an anatase phase. When the calcination temperature is increased, the crystalline structure of the titanium oxides in the Ti/B binary oxide catalyst caused the structure to change from an anatase phase to a rutile phase, while boron oxide species maintained an amorphous state. Pt-loaded Ti/B binary oxide exhibited the special photocatalytic activity for the stoichiometric decomposition of pure water in suspension systems. The decrease in the photocatalytic activity with the calcination temperature indicated that the photocatalytic activity of the Ti/B binary oxide for water decomposition was strongly dependent on the crystal

structure of the titanium oxide species in the Ti/B binary oxide. A remarkable yield in the reaction of water decomposition was obtained when Na_2CO_3 was added in the Pt-loaded Ti/B photocatalyst aqueous suspension.

Acknowledgements

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