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Nanocrystalline brookite-type titanium(IV) oxide photocatalysts prepared by a solvothermal method: correlation between their physical properties and photocatalytic activities

Hiroshi Kominami[a,b,*], Yoshinori Ishii[a], Masaaki Kohno[a], Shunsuke Konishi[a],
Yoshiya Kera[a,b], and Bunsho Ohtani[c]

[a]*Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University,*
Kowakae, Higashiosaka, Osaka 577-8502, Japan
[b]*Open Research Center, Kinki University, Kowakae, Higashiosaka, Osaka 577-8502, Japan*
[c]*Catalysis Research Center, Hokkaido University, Sapporo 060-0811, Japan*

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Nanocrystalline brookite-type titanium(IV) oxide (TiO_2) powder was synthesized by solvothermal treatment of oxobis(2,4-pentanedionato-O,O′)titanium in a 1,2-ethanediol-water system in the presence of sodium acetate followed by hydrothermal treatment at 373 K in order to remove organic moieties contaminating the powder. The powder was calcined at various temperatures to change its physical properties and then used for three types of photocatalytic reaction: mineralization of acetic acid (AcOH) in an aerated aqueous suspension of bare TiO_2 powder, evolution of molecular hydrogen from 2-propanol in an aqueous suspension of *in situ* platinized powder and formation of molecular oxygen (O_2) from silver sulfate in a deaerated aqueous suspension of bare TiO_2 powder. Dependence of the photocatalytic activities on calcination temperature (T_c) and correlations with the physical properties of brookite-type TiO_2 samples were examined. In the case of mineralization of AcOH, the uncalcined brookite TiO_2 sample having the largest surface area showed the highest rate of carbon dioxide evolution (R_{CO_2}), which was equal to that of representative commercial TiO_2 (Degussa P-25), and R_{CO_2} decreased monotonously with T_c, i.e., with decrease in surface area. On the other hand, in the case of O_2 formation, the photocatalytic activity was enhanced by calcination at a higher temperature, despite the simultaneous decrease in surface area. Overall, the effects of calcination on the photocatalytic activities for the three reaction systems strongly suggested that photocatalytic activity of brookite-type TiO_2 depends on two significant factors, adsorbability and recombination probability, corresponding to the specific surface area and crystallinity, respectively, and that the balance of these two factors determines T_c dependence.

KEY WORDS: titanium oxide; brookite; photocatalyst.

1. Introduction

Titanium(IV) oxide (TiO_2) is a promising photocatalyst because it generally exhibits levels of activity higher than those of other semiconductor photocatalysts in several reaction systems [1–7]. Inexpensiveness, excellent chemical stability and nontoxicity of TiO_2 make it attractive for practical applications. There are three crystal phases of TiO_2: anatase, rutile and brookite. The anatase and rutile phases have a tetragonal structure [8,9], while the brookite phase has an orthorhombic structure [10]. Anatase and rutile are synthesized by various methods, and there have been many studies on their photocatalysis [11–13]. However, there have only been a few studies on the synthesis of brookite-type TiO_2 [14–18]. To the best of our knowledge, there is only one report on the successful use of synthesized brookite TiO_2 as a photocatalyst. Ohtani *et al.* [19] found that brookite TiO_2 samples prepared by a procedure reported by Kiyama *et al.* [14] showed high levels of photocatalytic activity for both the reactions of molecular hydrogen (H_2) formation from 2-propanol (PrOH) and molecular oxygen (O_2) evolution from silver sulfate (Ag_2SO_4) in an aqueous suspension of TiO_2 under deaerated conditions. However, the correlation between photocatalytic activities and physical properties of brookite TiO_2 is still unclear. The difficulty in preparing pure brookite TiO_2 samples having various physical properties is probably one of the reasons for the small number of reports on photocatalysis of brookite TiO_2.

We have found that nanocrystalline brookite-type TiO_2 was synthesized in a 1,2-ethanediol-water system under a solvothermal condition [16]. The use of a combination of several characterization techniques revealed that the brookite-type TiO_2 product was free from contamination of other TiO_2 phases such as anatase, and the brookite crystallite in the product was preserved even after calcination at 973 K.

In the present study, we prepared brookite TiO_2 samples having various physical properties by calcining the brookite product, which had been synthesized by the

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[*] To whom correspondence should be addressed.

solvothermal method, at various temperatures and used them for three types of photocatalytic reactions in an aqueous suspension of brookite TiO_2, i.e., mineralization of acetic acid (AcOH) in an aerated aqueous suspension of bare TiO_2 powder, evolution of H_2 from 2-propanol in an aqueous suspension of *in situ* platinized powder and formation of O_2 from Ag_2SO_4 in a deaerated aqueous suspension of bare TiO_2 powder. Dependence of the photocatalytic activities on calcination temperature (T_c) and correlations with the physical properties of brookite-type TiO_2 samples are briefly described in this paper.

2. Experimental

2.1. Synthesis and characterization of brookite-type TiO_2 powders

Brookite-type TiO_2 powder was synthesized according to the procedure previously reported [16]. Oxobis(2,4-pentanedionato-O,O′)titanium ($TiO(acac)_2$, 0.019 mol) (Tokyo Kasei, Tokyo, Japan) and sodium acetate (0.038 mol) (Kanto Chemical, Tokyo, Japan) were added to 70 cm^3 of 1,2-ethanediol (ethylene glycol, EG) (Kanto Chemical) in a test tube, which was then set in a 200-cm^3 autoclave. In the gap between the test tube and the autoclave wall, 5 cm^3 of water (H_2O) was added. The autoclave was purged with nitrogen, heated to 573 K at a rate of 2.5 K min^{-1} and held at that temperature for 4 h. The product was washed first with acetone and then with methanol repeatedly under sonication and dried at 373 K under atmospheric pressure. As-synthesized brookite-type TiO_2 powder was contaminated with organic residue originating in solvent EG. To remove the organic moieties from the brookite product so as to prevent a drastic change in its physical properties, the product was treated under a hydrothermal condition at 373 K: the powder was suspended in 15 cm^3 of H_2O in a 25-cm^3 Teflon linear, which was sealed with a stainless frame and heated at 373 K for 24 h. The treated sample was washed with H_2O repeatedly and dried *in vacuo* at room temperature. The dried sample was calcined in a furnace at various temperatures under a flow of air (30 cm^3 min^{-1}); the sample was heated to a desired temperature at a rate of 10 K min^{-1}, kept at that temperature for 1 h and then cooled to room temperature in the furnace. Each of the thus-calcined samples is designated as brookite (T_c), e.g., a sample calcined at 973 K is designated as brookite (973).

Powder X-ray diffraction (XRD) (MultiFlex, Rigaku, Tokyo, Japan) was measured using Cu Kα radiation with a carbon monochromater. Crystallite size of brookite (d_{121}) was calculated from the half-height width of the 121 diffraction peak of brookite using the Scherrer equation. The value of the shape factor, K, was taken to be 0.9. The specific surface area (S_{BET}) was calculated using the BET single-point method on the basis of nitrogen (N_2) uptake measured at 78 K at the relative pressure of 0.3. Before the N_2 adsorption, each sample was dried at 403 K for 30 min in a 30% N_2-helium flow. Thermogravimetry (TG) (TG-8120, Rigaku) was carried out at a rate of 10 K min^{-1} in airflow.

2.2. Photocatalytic reaction in an aqueous suspension of brookite TiO_2

Three types of photocatalytic reactions were examined to evaluate the activities of brookite TiO_2 samples having various physical properties: (1) for photocatalytic reaction in an aqueous AcOH solution, bare TiO_2 powder (50 mg) was suspended in an AcOH solution (175 μmol, 5.0 cm^3), (2) for photocatalytic reaction in an aqueous Ag_2SO_4 solution, bare TiO_2 powder (50 mg) was suspended in an Ag_2SO_4 solution (125 μmol, 5.0 cm^3) and (3) for photocatalytic reaction in an aqueous 2-PrOH solution, Pt (0.1 wt%)-TiO_2 powder (50 mg) was suspended in a 2-PrOH solution (500 μmol, 5.0 cm^3). The reaction of (1) was carried out in reaction tubes (each 18 mm in diameter and 180 mm in length, transparent for light of wavelength >300 nm) under aerated conditions, while the reactions of (2) and (3) were carried out under an argon atmosphere. For the reaction of (3), platinization of TiO_2 was performed by *in situ* photochemical deposition method [20]. A solution (30 mm^3) of tetraamineplatinum(II) chloride ($[Pt(NH_3)_4]Cl_2$, Wako Chemical, 1.52 mg-Pt cm^{-3}) was injected in the 2-PrOH solution. The tube was sealed with a rubber septum and then photoirradiated at $\lambda > 300$ nm by a 400-W high-pressure mercury arc (Eiko-sha, Osaka, Japan) with magnetic stirring (1000 rpm) at 298 K. After the irradiation, the amounts of H_2, O_2 and carbon dioxide (CO_2) in the gas phase of reaction mixtures were measured using a Shimadzu GC-8A gas chromatograph equipped with MS-5A (O_2 and H_2) and Porapak QS (CO_2) columns. The amounts of 2-PrOH and acetone were analyzed with a Shimadzu GC-8A gas chromatograph equipped with an FID and a column packed with PEG20M. Deposited silver was analyzed by inductively coupled plasma emission spectroscopy (ICP, Shimadzu ICPS-1000III) after dissolution with concentrated nitric acid (HNO_3). Prior to the photocatalytic reaction of the uncalcined sample, pretreatment was carried out in order to completely eliminate contaminated organic species on the TiO_2 surface; TiO_2 powder (50 mg) was suspended in 5 cm^3 of water in a glass test tube and photoirradiated in the same way under O_2 with magnetic stirring until CO_2 was no longer liberated. In all reaction systems, photoactivities of representative active TiO_2 (Degussa P-25) were also determined to compare the activities of the brookite TiO_2 samples.

3. Results and discussion

3.1. Hydrothermal treatment of nanocrystalline brookite-type TiO_2 powder synthesized by the solvothermal method using EG-H_2O medium

In the XRD pattern and FT-Raman spectrum of the sample after hydrothermal treatment at 373 K, another phase such as anatase was not observed, indicating that the amount of amorphous-like phase to be crystallized to anatase form under the hydrothermal condition was negligible. Figure 1 and table 1 show TEM photographs and d_{121} of the brookite samples before and after the hydrothermal treatment, respectively. Apparent change was not seen in either particle size observed by TEM or d_{121} determined by XRD, indicating that the hydrothermal treatment at this temperature did not alter the crystallinity of the original brookite nanocrystals. Table 1 also summarizes results of TG of samples before and after the hydrothermal treatment. In the range from room temperature to 450 K, weight loss (1.4%), which is attributed to desorption of H_2O, of the untreated sample was smaller than that of the treated sample (3.2%). In the range of temperatures between 450 and 700 K, the untreated sample exhibited 3.7% weight loss

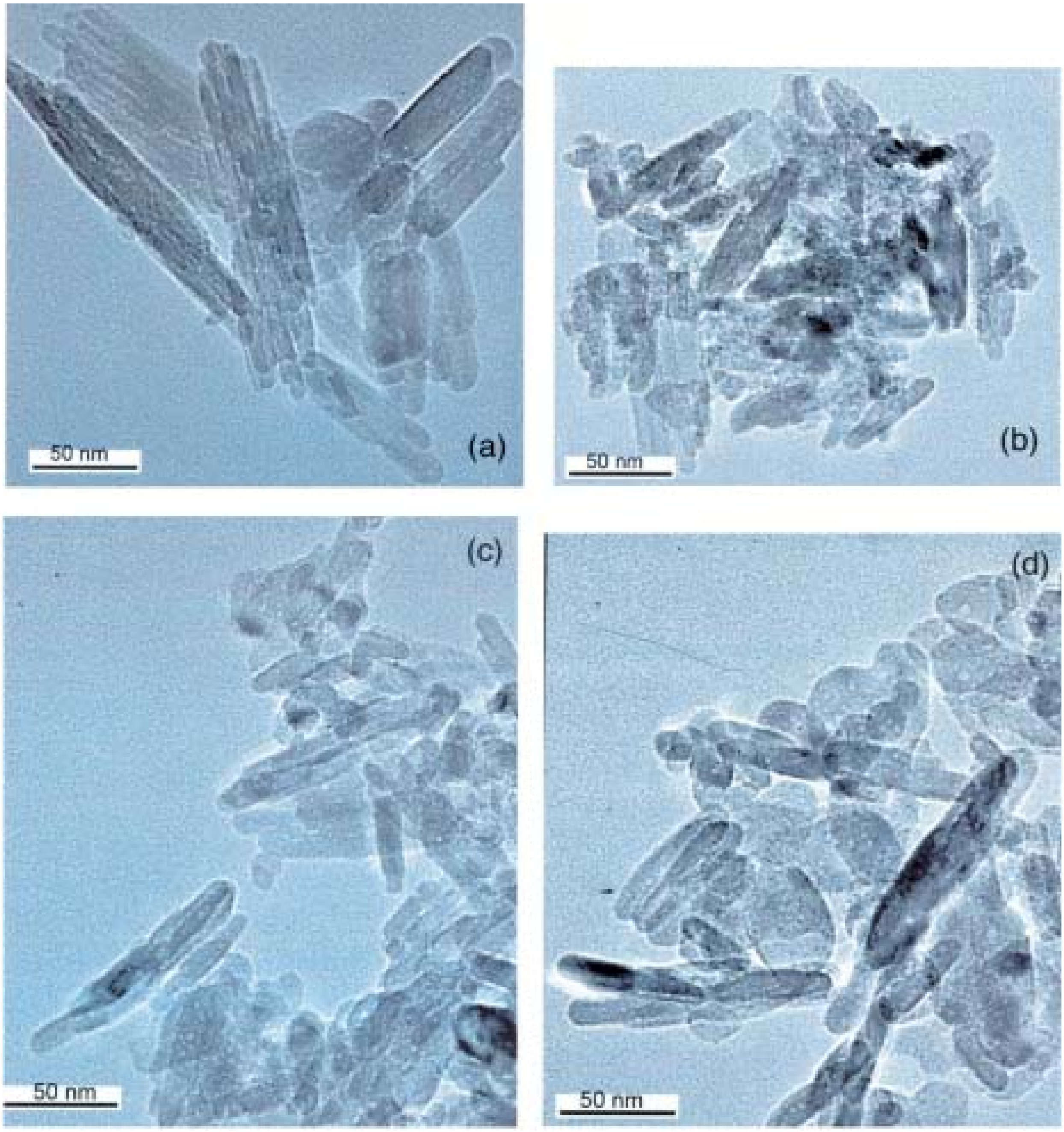

Figure 1. TEM photographs of brookite samples (a) before and (b) after hydrothermal treatment at 373 K for 24 h and of samples obtained by calcination of the hydrothermal product at (c) 873 K and (d) 973 K.

Table 1
Effect of hydrothermal treatment (HT) on physical properties of nanocrystalline brookite TiO_2 synthesized by solvothermal treatment

HT at 373 K	Weight loss[a] (%)			d_{121}[c] (nm)	S_{BET} (m^2g^{-1})
	rt-450 (K)	450–700 (K)	Total[b]		
Before	1.4	3.7	6.2	15	79
After	3.2	1.9	6.0	14	90

[a] Determined by thermogravimetry.
[b] Total weight loss from rt to 1273 K.
[c] Crystallite size calculated from the 121 diffraction peak of brookite.

mainly due to combustion of organic moieties, whereas the treated sample exhibited 1.9% weight loss. These results indicate that organic moieties contaminating the original brookite TiO_2 were partially removed from the particles by replacement with H_2O under the hydrothermal condition. S_{BET} was slightly increased from 79 to $90\,m^2\,g^{-1}$ after mild hydrothermal treatment due to removal of organic residue without a decrease in surface area of the brookite sample. In the FTIR spectrum of the sample obtained by hydrothermal treatment at 473 K, peaks assignable to EG moieties tethered to brookite particles were not observed.

3.2. Preparation of brookite TiO_2 samples having various physical properties

Hydrothermally treated brookite-type TiO_2 samples were calcined at various T_c. Figure 2 shows XRD patterns of the thus-obtained samples. The brookite crystallite was preserved even after calcination at 973 K and partially transformed into rutile crystallite at 1073 K. Figure 3 shows the effects of T_c on crystallite size and S_{BET} of these brookite samples. An uncalcined brookite sample only dried at 373 K (brookite(373)) exhibited a small crystallite size (14 nm) and a large S_{BET} ($90\,m^2\,g^{-1}$) as shown in the previous section. Crystallite size of brookite gradually increased, but S_{BET} decreased with increase in T_c. However, the brookite sample still exhibited a small d_{121} (17 nm) and a sufficient S_{BET} ($55\,m^2\,g^{-1}$) even after calcination at 973 K. Sufficient crystallinity of the brookite sample after hydrothermal treatment is attributed to its greater thermal stability. Therefore, brookite samples having various physical properties could be prepared by calcination of hydrothermally treated samples at various temperatures. Figure 1(c) and (d) shows TEM photographs of these brookite samples, indicating that the average particle size increased with elevation in T_c, which is consistent with the change in d_{121}. A similar gradual change in physical properties upon calcination was observed in nanocrystalline, anatase-type TiO_2 samples prepared by several solvothermal methods [21–24].

3.3. Photocatalytic activities and their correlation with physical properties

Thus-prepared brookite TiO_2 samples were used for three kinds of photocatalytic reaction. First, photocatalytic mineralization of AcOH in an aqueous suspension of a brookite sample was examined. This reaction system has been studied extensively [25,26], and complete decomposition of AcOH to CO_2 occurred as shown below.

$$CH_3COOH + 2O_2 = 2CO_2 + 2H_2O$$

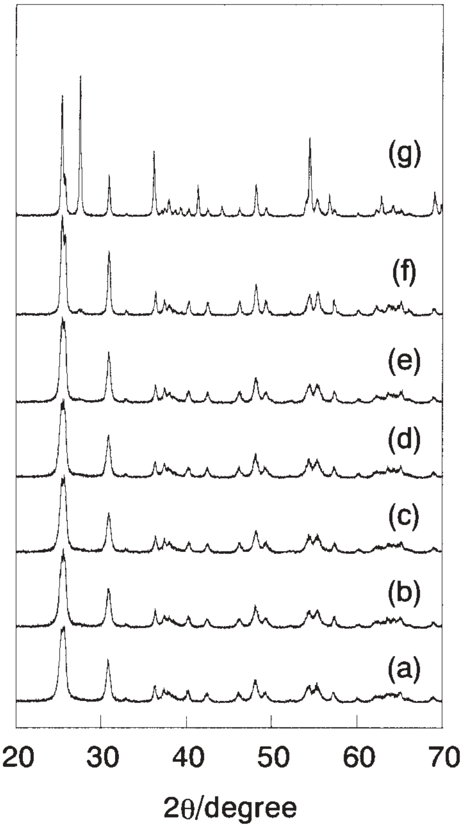

Figure 2. XRD patterns of (a) a hydrothermally treated brookite-type TiO_2 sample and of samples obtained by calcination of the hydrothermal product at (b) 623 K, (c) 773 K, (d) 873 K, (e) 973 K, (f) 1073 K and (g) 1173 K.

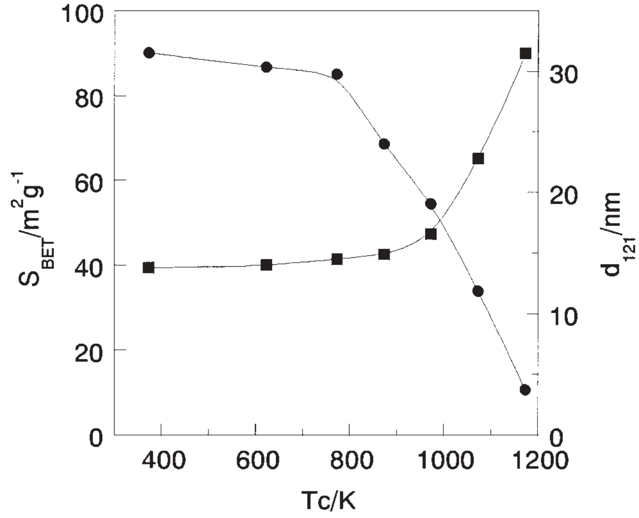

Figure 3. Effects of calcination temperature (T_c) on crystallite size and S_{BET} of brookite samples.

Figure 4(a) shows the effect of T_c on the CO_2 evolution rate. Brookite(373) with the largest S_{BET} exhibited the largest CO_2 evolution rate (22 μmol h^{-1}). It should be noted that the rate is equal to that of P-25 TiO_2 (22 μmol h^{-1}). This is a first report clarifying that brookite-type TiO_2, as well as anatase-type TiO_2, exhibited sufficient photocatalytic activity in a photocatalytic mineralization system under aerated conditions. The CO_2 evolution rate monotonously decreased as T_c increased, a tendency similar to that of S_{BET} of brookite samples. The effect of T_c on adsorption of AcOH was previously examined in TiO_2 prepared by a solvothermal method, and a linear correlation between specific surface area and amount of AcOH adsorbed was observed independent of the crystal structure of TiO_2 and the preparation method [27]. Similarly, in the case of the present brookite samples, the amount of AcOH adsorbed probably decreased with elevation in T_c, corresponding to S_{BET}. Crystallinity of brookite samples should be improved with increase in T_c, i.e., surface defects were diminished (annealing effect), resulting in a decrease in the probability of recombination of an electron–hole pair (e^-–h^+), because surface defects on crystals induce the recombination of e^-–h^+ [28]. Therefore, calcination has both positive and negative effects on photocatalytic activity of brookite TiO_2. The results obtained in this experiment clearly indicate that, in this reaction system, surface area of brookite TiO_2, i.e., adsorptivity toward AcOH, was more important than crystallinity that affects recombination properties of TiO_2. The same effect of T_c on the CO_2 evolution rate was observed in the case of nanocrystalline anatase-type TiO_2 samples prepared by solvothermal methods [23,24,29].

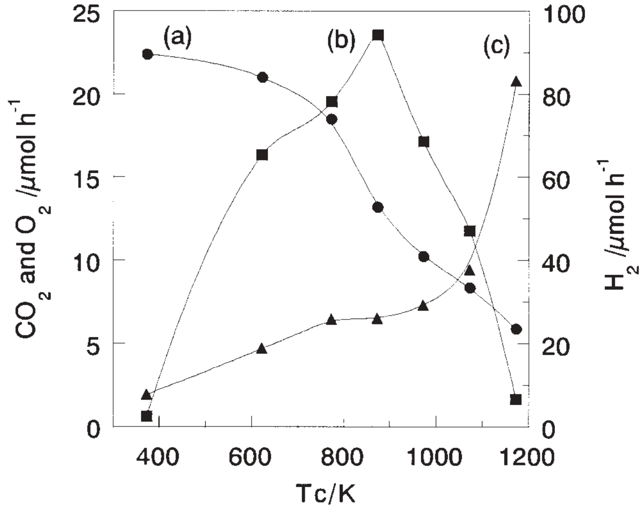

Figure 4. Effect of calcination temperature (T_c) on photocatalytic reaction rates for (a) CO_2 evolution, (b) H_2 evolution, and (c) O_2 evolution from acetic acid, 2-propanol and silver sulfate in aqueous suspensions of brookite TiO_2, respectively. Details about the reaction conditions were described in the experimental section.

The brookite samples of various physical properties were used for the photocatalytic evolution of H_2 from PrOH in an aqueous suspension of platinized TiO_2 under deaerated conditions ($CH_3CH(OH)CH_3 = CH_3COCH_3 + H_2$). This reaction system has also been studied extensively, and it has been shown that deposition of platinum on TiO_2 particles is necessary for continuous evolution of H_2 [30,31]. Figure 4(b) shows the effect of T_c on the H_2 evolution rate. Brookite(373) having the largest S_{BET}, which was most active in the mineralization of AcOH, showed a low rate of H_2 evolution (10 μmol h^{-1}). The rate of H_2 evolution increased with elevation in T_c, and brookite(873) exhibited the highest rate (94 μmol h^{-1}), which is almost comparable to that of TiO_2 P-25 (99 μmol h^{-1}). The formation of H_2 clearly indicates that the potential of the conduction band edge of brookite-type TiO_2 is negative for the potential of H_2 formation, H^+/H_2 (0 V at pH 0). Graetel and Rotzinger estimated the band-gap energies and flat-band potential of brookite to be 3.14 eV and ca. -0.03 V [32]. The latter value is consistent with the present experimental results. Further elevation in T_c, however, resulted in a decrease in the rate probably due to the large decrease in S_{BET}. An anatase-type TiO_2 sample with improved crystallinity by calcination but still having a relatively large surface area exhibited the highest rate among them [23,24,27,31], suggesting that both adsorptivity and crystallinity determine the activity of TiO_2 in the H_2 evolution system independent of the crystal structure.

Figure 4(c) shows the effect of T_c on O_2 evolution from an Ag_2SO_4 solution. This photocatalytic reaction system has also been studied well [33,34], and the stoichiometric reaction proceeds as follows: $4Ag^+ + 2OH = 4Ag + O_2 + 2H^+$. Large-surface-area brookite(373) exhibited negligible O_2 evolution, and the O_2 yield monotonically increased with elevation in T_c. The same effect of T_c was observed in anatase-type TiO_2 samples prepared by solvothermal methods [27,35]. Results for brookite and anatase TiO_2 samples show that improvement in crystallinity by calcination is effective for the O_2 evolution system. In this system, four holes should reach the same reaction site, escaping from recombination with a photogenerated electron, in order to form O_2 by oxidation of surface-adsorbed water or a surface hydroxyl group, suggesting that recombination probability is a decisive factor in the O_2 evolution system. Results obtained by using several evaluation methods have shown that calcination reduced the recombination probability of e^-–h^+ in anatase and rutile TiO_2 powders [36,37], indicating that T_c has a positive effect on O_2 evolution.

4. Conclusions

The physical properties (e.g. surface area and particle size) of nanocrystalline brookite-type TiO_2 powders, which had been synthesized by a solvothermal method followed by hydrothermal treatment, could be successfully controlled over a wide range by changing the postcalcination temperature (T_c) up to 1173 K. The effects of calcination on photocatalytic activities for several photocatalytic reactions were studied, and it was found that the activities strongly depend on the extents of two significant physical factors for active photocatalysts: surface area (adsorbability) and crystallinity (recombination probability). The brookite sample having the largest surface area exhibited a rate of carbon dioxide formation comparable to that of Degussa P-25 TiO_2, and another sample with both sufficient surface area and improved crystallinity showed almost the same rate of hydrogen formation as that of P-25. These results obtained for brookite samples clearly show that brookite-type TiO_2 possesses sufficient potential as a photocatalyst. The degrees of dependence of brookite TiO_2 on T_c in three reaction systems were different, but the dependence on T_c in each reaction system was almost the same as that of anatase-type TiO_2 prepared by several solvothermal methods. The difference in the degrees of T_c dependence of anatase TiO_2 in three reactions can be explained by the number of electrons (or holes) required to complete the photocatalytic reaction; the larger the number becomes, the more the recombination probability affects the reaction rate [27,35]. Thus, our interpretation might be applied for brookite TiO_2, although we did not examine adsorption properties of brookite samples. These results for brookite and anatase TiO_2 samples may provide important information for the design and synthesis of a highly active semiconductor photocatalyst by taking the reaction types into consideration.

Acknowledgments

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References

[1] N. Sepone and E. Pelizzetti (eds), *Photocatalysis: Fundamentals and Applications* (John Wiley Sons, New York, 1989).
[2] D.F. Ollis and H. Al-Ekabi (eds), *Photocatalytic Purification and Treatment of Water and Air* (Elsevier, Amsterdam, 1993).
[3] P.V. Kamat, Chem. Rev. 93 (1993) 267.
[4] M.A. Fox and M.T. Dulay, Chem. Rev. 93 (1993) 341.
[5] M.R. Hoffmann, S.T. Martin, W. Choi and D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
[6] M. Schiavello (ed), *Heterogeneous Photocatalysis* (John Wiley Sons, New York, 1997).
[7] M. Kaneko and I. Okura (eds), *Photocatalysis: Science and Technology* (Kodansya Scientific, Tokyo, 2002).
[8] ICDD Card No. 21-1272.
[9] ICDD Card No. 21-1276.
[10] ICDD Card No. 29-1360.
[11] A. Mills and G.J. Porter, J. Chem. Soc., Faraday Trans. 1 78 (1982) 3659.
[12] S.-i. Nishimoto, B. Ohtani, H. Kajiwara and T. Kagiya, J. Chem. Soc., Faraday Trans. 1, 81 (1985) 61.
[13] R.I. Bickley, T. Gonzalez-Carreno, J.S. Lees, L. Palmisano and R.J.D. Tilley, J. Solid State Chem. 92 (1991) 178.
[14] M. Kiyama, T. Akita, Y. Tsutsumi and T. Takada, Chem. Lett. (1972) 21.
[15] T. Mitsuhashi and M. Watanabe, Miner. J. 9 (1978) 236.
[16] H. Kominami, M. Kohno and Y. Kera, J. Mater. Chem. 10 (2000) 1151.
[17] Y. Zheng, E. Shi, S. Cui, W. Li and X. Hu, J. Am. Ceram. Soc. 83 (2000) 2634.
[18] A. Pottier, C. Chaneac, E. Tronc, L. Mazerolles and J.-P. Jolivet, J. Mater. Chem. 11 (2001) 1116.
[19] B. Ohtani, J.-i. Handa, S.-i. Nishimoto and T. Kagiya, Chem. Phys. Lett. 120 (1985) 292.
[20] B. Kraeutler and A.J. Bard, J. Am. Chem. Soc. 100 (1978) 4317.
[21] H. Kominami, Y. Takada, H. Yamagiwa, Y. Kera, M. Inoue and T. Inui, J. Mater. Sci. Lett. 15 (1996) 197.
[22] H. Kominami, M. Kohno, Y. Takada, M. Inoue, T. Inui and Y. Kera, Ind. Eng. Chem. Res. 38 (1999) 3925.
[23] H. Kominami, J.-i. Kato, Y. Takada, Y. Doushi, B. Ohtani, S.-i. Nishimoto, M. Inoue, T. Inui and Y. Kera, Catal. Lett. 46 (1997) 235.
[24] H. Kominami, J.-i. Kato, S.-y. Murakami, Y. Kera, M. Inoue, T. Inui and B. Ohtani, J. Mol. Catal. A 144 (1999) 165.
[25] K. Kato, A. Tsuzuki, Y. Torii, H. Taoda, T. Kato and Y. Butsugan, J. Mater. Sci. 30 (1995) 837.
[26] H. Kominami, J.-i. Kato, M. Kohno, Y. Kera and B. Ohtani, Chem. Lett. (1996) 1051.
[27] H. Kominami, S.-y. Murakami, J.-i. Kato, Y. Kera and B. Ohtani, J. Phys. Chem. B 106 (2002) 10501.
[28] P.T. Landsberg, *Recombination in Semiconductors* (Cambridge University Press, Cambridge, 1991) p. 208.
[29] H. Kominami, J.-i. Kato, M. Kohno, Y. Kera and B. Ohtani, Chem. Lett. (1996) 1051.
[30] S.-i. Nishimoto, B. Ohtani, and T. Kagiya, J. Chem. Soc., Faraday Trans. 1, 81 (1985) 2467.
[31] H. Kominami, T. Matsuura, K. Iwai, B. Ohtani, S.-i. Nishimoto and Y. Kera, Chem. Lett. (1995) 693.
[32] M. Graetel and F. Rotzinger, Chem. Phys. Lett. 118 (1985) 474.

[33] B. Ohtani, Y. Okugawa, S.-i. Nishimoto and T. Kagiya, J. Phys. Chem. 91 (1987) 3350.

[34] B. Ohtani and S.-i. Nishimoto, J. Phys. Chem. 97 (1993) 920.

[35] H. Kominami, S.-y. Murakami, Y. Kera and B. Ohtani, Catal. Lett. 56 (1998) 125.

[36] B. Ohtani, R.M. Bowman, D.P. Colombo Jr., H. Kominami, H. Noguchi and K. Uosaki, Chem. Lett. (1998) 579.

[37] S. Ikeda, N. Sugiyama, S.-i. Murakami, H. Kominami, Y. Kera, H. Noguchi, K. Uosaki, T. Torimoto and B. Ohtani, Phys. Chem. Chem. Phys. 5 (2003) 778.