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

Short title

Photocatalysis of Brookite TiO₂

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Nanocrystalline brookite-type titanium(IV) oxide (TiO₂) 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 TiO₂ powder, evolution of molecular hydrogen from 2-propanol in an aqueous suspension of in situ platinized powder, and formation of molecular oxygen (O₂) from silver sulfate in a deaerated aqueous suspension of bare TiO₂ powder. Dependence of the photocatalytic activities on calcination temperature (T_c) and correlations with the physical properties of brookite-type TiO₂ samples were examined. In the case of mineralization of AcOH, the uncalcined brookite TiO₂ sample having the largest surface area showed the highest rate of carbon dioxide evolution (R_{CO₂}), which was equal to that of representative

commercial TiO₂ (Degussa P-25), and R_{CO₂} decreased monotonously with T_c, i.e., with decrease in surface area. On the other hand, in the case of O₂ 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 TiO₂ 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 (TiO₂) 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 non-toxicity of TiO₂ make it attractive for practical applications. There are three crystal phases of TiO₂: 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 TiO₂ [14-18]. To the best of our knowledge, there is only one report on the successful use of synthesized brookite TiO₂ as a photocatalyst. Ohtani *et al.* [19] found that brookite TiO₂ samples prepared by a procedure reported by Kiyama *et al.* [14] showed high levels of photocatalytic activity for both the reactions of molecular hydrogen (H₂) formation from 2-propanol (PrOH) and molecular oxygen (O₂) evolution from silver sulfate (Ag₂SO₄) in an aqueous suspension of TiO₂ under deaerated conditions. However, the correlation between photocatalytic activities and physical properties of brookite TiO₂ is still unclear. Difficulty in preparing pure brookite TiO₂ samples having various physical properties is probably one of the reasons

for the small number of reports on photocatalysis of brookite TiO₂.

We have found that nanocrystalline brookite-type TiO₂ 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 TiO₂ product was free from contamination of other TiO₂ 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 TiO₂ samples having various physical properties by calcining the brookite product, which had been synthesized by the solvothermal method, at various temperatures and used them for three types of photocatalytic reactions in an aqueous suspension of brookite TiO₂, i.e., mineralization of acetic acid (AcOH) in an aerated aqueous suspension of bare TiO₂ powder, evolution of H₂ from 2-propanol in an aqueous suspension of in situ platinized powder, and formation of O₂ from Ag₂SO₄ in a deaerated aqueous suspension of bare TiO₂ powder. Dependence of the photocatalytic activities on calcination temperature (T_c) and correlations with the physical properties of brookite-type TiO₂ samples are briefly described in this paper.

2 Experimental

2.1 Synthesis and characterization of brookite-type TiO₂ powders

Brookite-type TiO₂ 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 cm³ of 1,2-ethanediol (ethylene glycol, EG) (Kanto Chemical) in a test tube, which was then set in a 200 cm³ autoclave. In the gap between the test tube and the autoclave wall, 5 cm³ of water (H₂O) 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 TiO₂ 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 cm³ of H₂O in a 25 cm³ Teflon linear, which was sealed with a stainless frame and heated at 373 K for 24 h. The treated sample was washed with H₂O 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 cm³ 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 thus-calcined samples is designated as brookite(Tc), 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 CuK α radiation with a carbon monochromator. 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 (N₂) uptake measured at 78 K at the relative pressure of 0.3. Before the N₂ adsorption, each sample was dried at 403 K for 30 min in a 30% N₂-helium flow. Thermogravimetry (TG) (TG-8120, Rigaku) was carried out at a rate of 10 K min⁻¹ in air flow.

2.2 Photocatalytic reaction in an aqueous suspension of brookite TiO₂

Three types of photocatalytic reaction were examined to evaluate the activities of brookite TiO₂ samples having various physical properties: (A) for photocatalytic reaction in an aqueous AcOH solution, bare TiO₂ powder (50 mg) was suspended in an AcOH solution (175 μmol , 5.0 cm³), (B) for photocatalytic reaction in an aqueous Ag₂SO₄ solution, bare TiO₂ powder (50 mg) was suspended in a Ag₂SO₄ solution (125 μmol , 5.0 cm³), and (C) For photocatalytic reaction in an aqueous 2-PrOH solution, Pt (0.1 wt%)-TiO₂ powder (50 mg) was suspended in a 2-PrOH solution (500 μmol , 5.0 cm³). The reaction of (A) 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 (B) and (C) were carried out under an Ar atmosphere. For the reaction of (C), platinization of TiO₂ was performed by in situ photochemical deposition method [20]. A solution (30 mm³) of tetraammineplatinum(II) chloride ([Pt(NH₃)₄]Cl₂, 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 H₂, O₂ and carbon dioxide (CO₂) in the gas phase of reaction mixtures were measured using a Shimadzu GC-8A gas chromatograph equipped with MS-5A (O₂ and H₂) and Porapak QS (CO₂) 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 Ag was analyzed by inductively coupled plasma emission spectroscopy (ICP, Shimadzu ICPS-1000III) after dissolution with concentrated nitric acid (HNO₃). Prior to the photocatalytic reaction of the uncalcined sample, pre-treatment was carried out in order to completely eliminate contaminated organic species on the TiO₂ surface; TiO₂ powder (50 mg) was suspended in 5 cm³ of water in a glass test tube and photoirradiated in the same way under O₂ with magnetic stirring until CO₂ was no longer liberated. In all reaction systems, photo-activities of representative active TiO₂ (Degussa P-25) were also determined to compare the activities of the brookite TiO₂ samples.

3 Results and Discussion

3.1 Hydrothermal treatment of nanocrystalline brookite-type TiO₂ powder synthesized by the solvothermal method using EG-H₂O 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 nano-crystals. **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 H₂O, 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 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 TiO₂ were partially removed from the particles by replacement with H₂O under the hydrothermal condition. S_{BET} was slightly increased from 79 to 90 m²g⁻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 TiO₂ samples having various physical properties

Hydrothermally treated brookite-type TiO₂ 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 m²g⁻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 m²g⁻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 d₁₂₁. A similar gradual change in physical properties upon calcination was observed in nanocrystalline, anatase-type TiO₂ samples prepared by several solvothermal methods [21-24].

3.3 Photocatalytic activities and their correlation with physical properties

Thus-prepared brookite TiO₂ 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 CO₂ occurred as shown below.

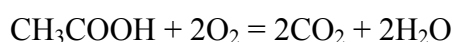


Figure 4 (a) shows the effect of T_c on the CO₂ evolution rate. Brookite(373) with the largest S_{BET} exhibited the largest CO₂ evolution rate (22 μmol h⁻¹). It should be noted that the rate is equal to that of P-25 TiO₂ (22 μmol h⁻¹). This is a first report clarifying that brookite-type TiO₂, as well as anatase-type TiO₂, exhibited sufficient photocatalytic activity in a photocatalytic mineralization system under aerated conditions. The CO₂ 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 TiO₂ 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 TiO₂ 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 TiO₂. The results obtained in this experiment clearly indicate that, in this reaction system, surface area of brookite TiO₂, i.e., adsorptivity toward AcOH, was more important than crystallinity that affects recombination properties of TiO₂. The same effect of Tc on the CO₂ evolution rate was observed in the case of nanocrystalline anatase-type TiO₂ samples prepared by solvothermal methods [23,24,29].

The brookite samples of various physical properties were used for photocatalytic evolution of H₂ from PrOH in an aqueous suspension of platinized TiO₂ 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 Pt on TiO₂ particles is necessary for continuous evolution of H₂ [30,31]. **Figure 4 (b)** shows the effect of Tc on the H₂ evolution rate. Brookite(373) having the largest S_{BET}, which was most active in mineralization of AcOH, showed a low rate of H₂ evolution (10 μmol h⁻¹). The rate of H₂ evolution increased with elevation in Tc, and brookite(873) exhibited the highest rate (94 μmol h⁻¹), which is almost comparable to that of TiO₂ P-25 (99 μmol h⁻¹). Formation of H₂ clearly indicates that the potential of the conduction band edge of brookite-type TiO₂ is negative for the potential of H₂ formation, H⁺/H₂ (0 V at pH 0). Graetzel 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 Tc, however, resulted in a decrease in the rate probably due to the large decrease in S_{BET}. An anatase-type TiO₂ 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 TiO₂ in the H₂ evolution system independent of the crystal structure.

Figure 4 (c) shows the effect of Tc on O₂ evolution from an Ag₂SO₄ solution. This photocatalytic reaction system has also been studied well [33,34], and stochiometric

reaction proceeds as follows: $4\text{Ag}^+ + 2\text{OH}^- = 4\text{Ag} + \text{O}_2 + 2\text{H}^+$. Large-surface-area brookite(373) exhibited negligible O₂ evolution, and O₂ yield monotonically increased with elevation in Tc. The same effect of Tc was observed in anatase-type TiO₂ samples prepared by solvothermal methods [27,35]. Results for brookite and anatase TiO₂ samples show that improvement in crystallinity by calcination is effective for the O₂ evolution system. In this system, four holes should reach the same reaction site, escaping from recombination with a photogenerated electron, in order to form O₂ by oxidation of surface-adsorbed water or a surface hydroxyl group, suggesting that recombination probability is a decisive factor in the O₂ evolution system. Results obtained by using several evaluation methods have shown that calcination reduced the recombination probability of e⁻-h⁺ in anatase and rutile TiO₂ powders [36,37], indicating that Tc has a positive effect on O₂ evolution.

Conclusions

The physical properties (e.g., surface area and particle size) of nanocrystalline brookite-type TiO₂ powders, which had been synthesized by a solvothermal method followed by hydrothermal treatment, could be successfully controlled over a wide range by changing the post-calcination temperature (Tc) 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 TiO₂, 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 TiO₂ possesses sufficient potential as a photocatalyst. The degrees of dependence of brookite TiO₂ on Tc in three reaction systems were different, but the dependence on Tc in each reaction system was almost the same as that of anatase-type TiO₂ prepared by several

solvothermal methods. The difference in the degrees of Tc dependence of anatase TiO₂ 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 TiO₂, although we did not examine adsorption properties of brookite samples. These results for brookite and anatase TiO₂ samples may provide important information for the design and synthesis of a highly active semiconductor photocatalyst by taking the reaction types into consideration.

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Figure captions

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.

Figure 2. XRD patterns of (a) a hydrothermally treated brookite-type TiO₂ 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. Effect of calcination temperature (T_c) on photocatalytic reaction rates for (a) CO₂ evolution, (b) H₂ evolution, and (c) O₂ evolution from acetic acid, 2-propanol, and silver sulfate in aqueous suspensions of brookite TiO₂, respectively. Details about the reaction conditions were described in the experimental section.