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Synthesis and photocatalytic activity of small brookite particles by self-hydrolysis of $TiOCl_2$

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The preparation of brookite particles was tried by self-hydrolysis of $TiOCl_2$ with HCl addition. When 0.1 M $TiOCl_2$ solution was heated at 100°C by reflux method, the precipitate was obtained within 15 min and was identified as brookite and anatase. By addition of HCl, the starting time of precipitation was delayed and small brookite formed beside rutile large rod particles. These results suggest that deprotonation at the early stage of reaction was suppressed but crystal growth at the late stage was promoted because of an increase in the solubility of TiO_2 sols.

When the $TiOCl_2$ solution was heated at 100°C for 24 h in autoclave, rutile large particles and brookite small particles formed separately. The small brookite particles could be separated by centrifugation. The photocatalytic activity of synthesized brookite particles was lower compared to commercial brookite particles. When hydrothermal treatment was carried out for synthesized brookite, the photocatalytic activity was enhanced. This was due to improvement of crystallinity of brookite.

Key-words : Brookite TiO_2, Small particles, Self-hydrolysis process, HCl addition, Separation

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1. Introduction

Titania (TiO_2) is widely used as white painting material, photocatalyst, gas sensor, solar cell and so on. Especially, TiO_2 nanoparticles have been receiving a lot of attention as photocatalyst. There are many attempts to prepare the TiO_2 crystalline nanoparticles by hydrothermal and solvothermal solution methods. Alkoxide method is one of the effective synthesis methods for monodispersed spherical particles. In the alkoxide method, spherical TiO_2 particles are synthesized and the particle size is $<1.0\,\mu m$.[1] Since TiO_2 powder synthesized in this method is ordinarily amorphous, the crystallization to rutile, brookite and/or anatase phase is usually carried out by thermal treatment. This process causes the particle agglomeration and the decrease in the specific surface area, retarding the photocatalytic activity. Crystalline TiO_2 particles are also synthesized by hydrothermal treatment of amorphous TiO_2 precipitate obtained by hydrolysis of titanium alkoxide[2],[3] or titanium salt.[4]–[6] In these processes, the crystalline phase and particle size can be changed by aging condition such as pH, temperature and pressure, but agglomeration of particles occurs.

Anatase phase is known to have high photocatalytic activity because of the wide band gap and the large surface area. On the other hand, there are a few works on brookite synthesis and its photocatalytic behavior, because the preparation of brookite particles is difficult in the single phase. Recently, brookite is receiving a lot of attention as photocatalyst and some researchers report the synthesis methods to obtain nanoparticles of brookite single phase. Brookite particles have been synthesized at least from 1970s and most of the reports describe that brookite forms besides rutile and/or anatase phase.[7]–[11] In order to obtain brookite single phase, the synthesis should be carried out at high temperature and pressure, such as by using autoclave, and proper heat treatment of as-synthesized powder is needed.[12] Some researchers obtained single crystalline brookite from Ti precursor solution.[13]–[18] S.-J. Kim et al. prepared transparent brookite sols from Ti peroxo solution.[13] Brookite single crystals were constructed from $[Ti_8O_{12}(H_2O)_{24}]Cl_8{\cdot}7H_2O$ as Ti precursor.[14] M. Kakihana et al. obtained brookite single phase from water-soluble Ti-complex nearly at neutral pH value.[15]–[18] However, even in these methods, the synthetic condition for brookite nanoparticles is limited and it is difficult to obtain brookite single phase.

In our group, the synthesis of TiO_2 by self-hydrolysis of $TiOCl_2$ has been studied.[19]–[23] Self-hydrolysis of $TiOCl_2$ is one of the effective processes to synthesize TiO_2 crystalline powders by one step. In our previous study, brookite nanoparticles brookite besides rutile can be synthesized from 0.1 M $TiOCl_2$ at 100°C with HCl addition by reflux method.[21] This agrees well with some reports using $TiOCl_2$ as Ti source.[24],[25] Y. Li et al. reported that bicrystalline titania of anatase and brookite with an average crystal size of below 10 nm was prepared from $TiOCl_2$ by adjusting the pH value of the starting solution.[24] J. H. Lee et al. also described that TiO_2 nanoparticles with a mixture of brookite and rutile phases were prepared from $TiOCl_2$.[25] In these reports, brookite was prepared but single crystalline of brookite was not obtained. In this study, we tried to investigate the effect of HCl addition by reflux and autoclave method on the synthesis of TiO_2 by self-hydrolysis of $TiOCl_2$ in order to obtain brookite nanoparticles. In addition, the photocatalytic activity of synthesized brookite was examined.

2. Experimental procedure

The synthesis of TiO_2 was carried out by the previous procedure.[9] The aqueous solution of $TiCl_4$ (16–17%Ti, Wako Pure Chemical Industries, Ltd.) was used as starting source. The $TiCl_4$ solution was diluted with deionized water in an ice bath to 0.1 M $TiOCl_2$. Hydrochloric acid (HCl; Nacalai Tesque, Inc. Wako Pure Chemical Industries, Ltd. Kishida Chemical Co.,

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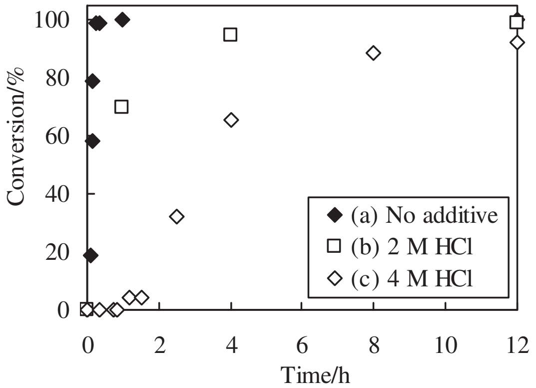

Fig. 1. Change in conversion of $TiOCl_2$ with time. The synthetic condition was set at 100°C from 0.1 M $TiOCl_2$ (a) without HCl, and with (b) 2 M HCl and (c) 4 M HCl addition.

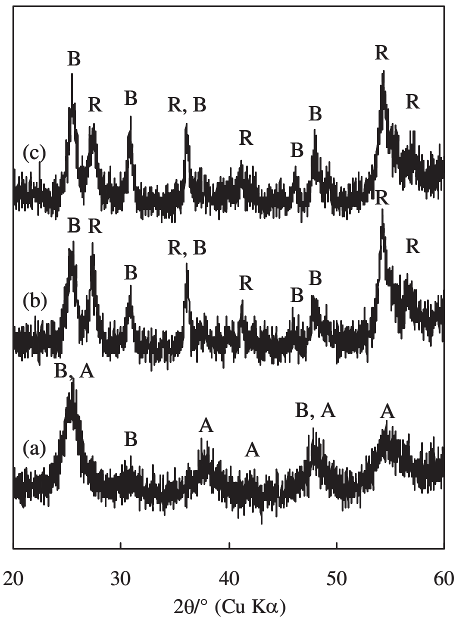

Fig. 2. XRD patterns of the products from 0.1 M $TiOCl_2$ at 100°C for 24 h by reflux method (a) without HCl, and with (b) 2 M HCl and (c) 4 M HCl addition; R: rutile, B: brookite, A: anatase.

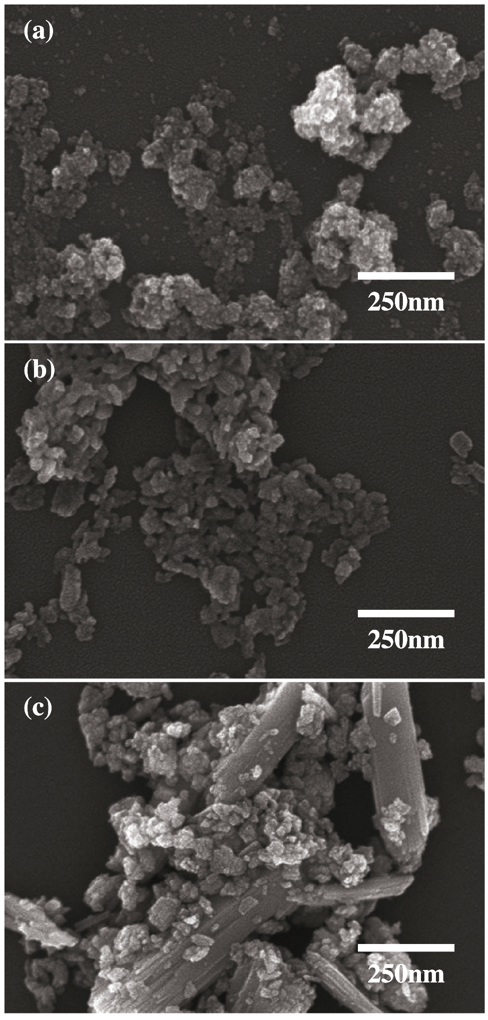

Fig. 3. SEM photographs of the products from 0.1 M $TiOCl_2$ at 100°C for 24 h by reflux method (a) without HCl, and with (b) 2 M HCl and (c) 4 M HCl addition.

Ltd.) was added to 0.1 M $TiOCl_2$ solution in order to control the pH value in starting solution. The concentration of HCl was set at 2–4 M. The starting solution (40 ml) was heated at 100°C for 1–24 h by reflux or autoclave method. After heating, the precipitate was separated by centrifugation. The produced powder was washed with deionized water and dried at 50°C.

The crystalline phases of TiO_2 powders were identified by X-ray diffraction (XRD; MiniFlex, Rigaku Co.) using Cu $K\alpha$ radiation (30 kV, 15 mA) and Raman spectrum analysis (NRS-2000, JASCO Co.). The particle morphology was observed by scanning electron microscopy (SEM; S-5200, Hitachi Co.). The N_2 adsorption isotherm was measured by BELSORP-mini II (BEL Japan, Inc.) and the specific surface area was calculated by BET method. The conversion of $TiOCl_2$ to TiO_2 was determined from the change in concentration of titanium ion in the supernatant solution after separation of the precipitate by centrifugation. The supernatant solution was colored by addition of H_2O_2 forming the complex with titanium ions, and the absorption spectrum was measured at $\lambda = 408.90$ nm with a UV–Visible spectrometer (U-3300, Hitachi Co.). The photocatalytic activity of the brookite particles was determined by degradation of methylene-blue (MB) in water. The 20 mg of powder sample was suspended in 100 ml of 50 µM MB aqueous solution. The change of MB concentration by adsorption was pursued for 18 h under dark condition, and then that by photocatalytic decomposition for 10 h under UV light irradiation (365 nm).

3. Results and discussion

3.1 Reflux method

First, the effect of HCl addition on the formation of TiO_2 was investigated from 0.1 M $TiOCl_2$ at 100°C for 24 h by reflux method. **Figure 1** shows the change in conversion of $TiOCl_2$ to TiO_2 with time. Without HCl, the conversion of $TiOCl_2$ reached nearly 100% at the early stage of reaction. When HCl was added to $TiOCl_2$, the rise of conversion was retarded. **Figure 2** shows the XRD patterns of products synthesized by reflux method with and without HCl. When 0.1 M $TiOCl_2$ was heated by reflux method, brookite and anatase formed. On the other hand, by addition of HCl, anatase peaks were not observed and brookite and rutile peaks were detected. As the concentration of HCl was higher, the peak intensity of brookite increased. The SEM images of products were shown in **Fig. 3**. By SEM, agglomerates of nanoparticles were observed without HCl. By addition of HCl, acicular and cuboidal particles formed and grew dispersively with an increase in HCl concentration.

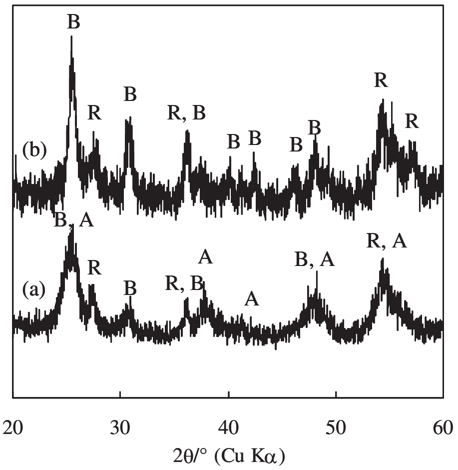

Fig. 4. XRD patterns of the products from 0.1 M $TiOCl_2$ at 100°C for 24 h by autoclave method with (b) and without (a) 2 M HCl; R: rutile, B: brookite, A: anatase.

We have already reported the formation mechanism of TiO_2 by self-hydrolysis of $TiOCl_2$.[9] First, deprotonation of $[Ti(OH)_2 \cdot 4H_2O]^{2+}$ complex proceeds in the solution and TiO_2 precursor, $[Ti(OH)_4 \cdot 2H_2O]$, is generated. Rutile nuclei and TiO_2 sols form by condensation-polymerization of $[Ti(OH)_4 \cdot 2H_2O]$, and then the crystal growth of rutile progresses by dissolution-reprecipitation of TiO_2 sol.

In this study, the rise in conversion of $TiOCl_2$ was retarded by addition of HCl, indicating the suppression of deprotonation. When the deprotonation is suppressed, rutile should form preferentially. However, in this study, brookite formed beside rutile. This result might be explained by the increase in solubility of TiO_2 sols at high HCl concentration. In addition, the XRD peaks of brookite and rutile became sharp and peak intensity increased with an increase in HCl concentration. These results suggest that the crystal growth of brookite and rutile through the dissolution–reprecipitation was promoted because of an increase in the solubility of TiO_2 sols.

3.2 Autoclave method

The effect of using autoclave under the presence of HCl was investigated from 0.1 M $TiOCl_2$ at 100°C for 24 h. Compared to reflux method, the starting time of precipitation was delayed regardless of HCl addition by autoclave method. Especially, precipitate was not obtained by addition of 4 M HCl. These results indicate that deprotonation was suppressed by using autoclave. When $TiOCl_2$ with HCl solution was heated by reflux method, HCl concentration decreased with time because of open system. On the other hand, by using autoclave, HCl concentration kept high, resulting in high solubility of TiO_2 sols. This causes the suppression of deprotonation.

Figure 4 shows the XRD patterns of products synthesized by autoclave method with and without 2 M HCl. In autoclave method, not only brookite and anatase, but also rutile peaks were detected even without HCl. By addition of 2 M HCl, anatase peaks disappeared and the peak intensity of brookite increased. By SEM, agglomerates of nanoparticles and acicular particles were observed without HCl, whereas large particles of the size of 4 µm, and cuboidal small particles of about 100 nm, formed with 2 M HCl addition. These results suggest that the crystal growth of brookite was promoted by using autoclave. This might be caused by high solubility of TiO_2 sols.

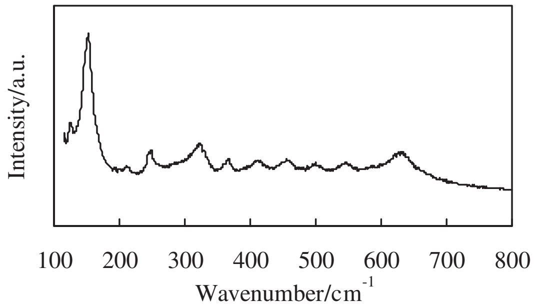

Fig. 5. Raman spectrum of the product after separation by centrifugation.

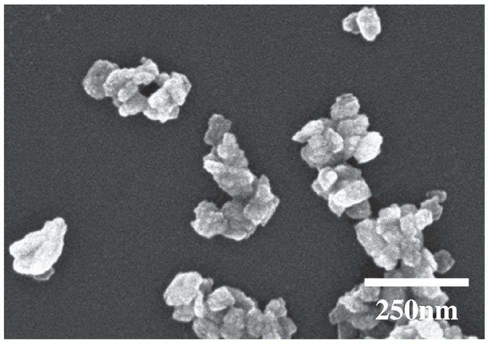

Fig. 6. SEM photographs of the products after separation by centrifugation.

3.3 Separation of brookite

In autoclave method, rutile large particles and brookite small particles were synthesized from 0.1 M $TiOCl_2$ with 2 M HCl addition. The rutile and brookite particles were dispersed well in the solution and separated by centrifugation. The separation procedure was as follows: After heating of starting solution at 100°C for 24 h, the suspension was centrifuged at 3000 rpm, resulting in the sedimentation of rutile large particles. Then, centrifugation at 12000 rpm was carried out, and only brookite particles were obtained. **Figures 5** and **6** show the Raman spectrum and SEM image of samples after centrifugation at 12000 rpm. Only brookite peaks were detected by Raman and small particles in the size of 100 nm were observed by SEM, indicating separation of brookite small particles proceeded successfully.

3.4 Photocatalytic activity

Figure 7 shows the change in MB concentration with time. Compared to commercial brookite powder (Kojundo Chemical Lab. Co., Ltd.), the synthesized brookite particles had higher adsorption ability for MB, but lower decomposition ability. This may be due to low crystallinity of synthesized brookite.

In order to enhance the crystallinity of synthesized brookite, the hydrothermal treatment was carried out. The synthesized brookite particles was dispersed to water or 0.1 M HCl solution, and then heated at 100 or 200°C for 24 h. **Figure 8** shows the XRD patterns samples before and after hydrothermal treatment. After hydrothermal treatment, only brookite peaks were detected and the peak intensity of brookite increased compared to as-synthesized. There was no change in the particle morphology even after hydrothermal treatment. However, the specific surface area became low by the treatment: 102 m^2/g in as-synthesized, 86 m^2/g at 100°C with water, 38 m^2/g at 200°C with water and

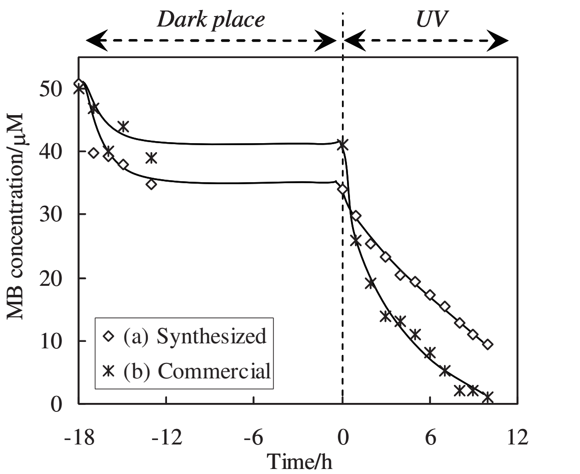

Fig. 7. Change in MB concentration with time. The samples were (a) synthesized brookite particles and (b) commercial brookite particles.

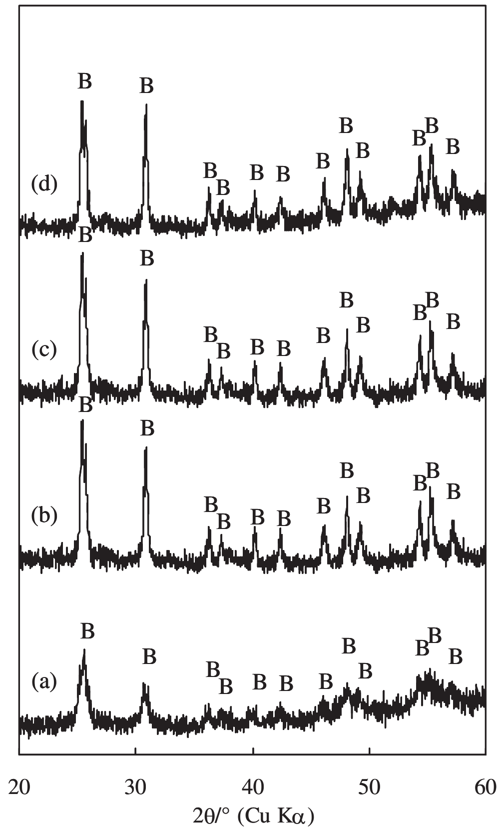

Fig. 8. XRD patterns of the products (a) before and after (b–d) hydrothermal treatment. The condition of hydrothermal treatment was set at (b) 100°C, (c) 200°C and (d) 200°C with 0.1 M HCl solution; B: brookite.

$36\,m^2/g$ at 200°C with 0.1 M HCl. These results suggest that the hydrothermal treatment was effective to enhance the crystallinity of brookite although the specific surface area decreased without particle growth.

Figure 9 shows the change in MB concentration with time by using the samples with hydrothermal treatment. Compared to as-synthesized, the samples with hydrothermal treatment had lower adsorption ability for MB. On the other hand, the decomposition of MB was promoted by hydrothermal treatment. These results

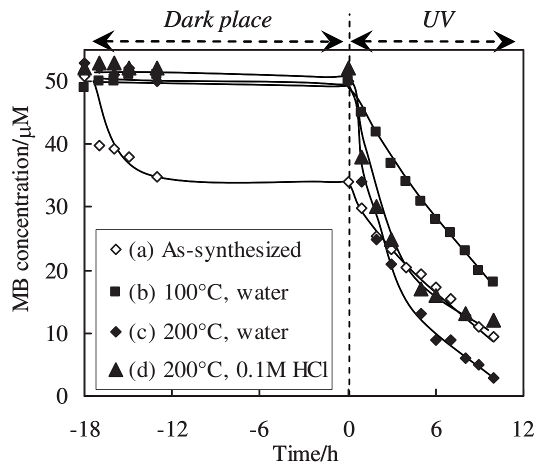

Fig. 9. Change in MB concentration with time. The samples were (a) as-synthesized and (b–d) hydrothermal treated brookite particles. The condition of hydrothermal treatment was set at (b) 100°C, (c) 200°C and (d) 200°C with 0.1 M HCl solution.

suggest that the adsorption ability was related to specific surface area, whereas the decomposition ability to crystallinity of samples. Anyway, photocatalytic activity of samples was improved by hydrothermal treatment of as-synthesized brookite.

4. Conclusions

We have studied on the synthesis of TiO_2 nanoparticles by self hydrolysis of $TiOCl_2$ in the aqueous solution, and found that the HCl addition had a significant effect on the formation of anatase, brookite and rutile phases. In the present work, the preparation of brookite particles was tried by self-hydrolysis of $TiOCl_2$ with HCl addition. When the $TiOCl_2$ solution was heated by reflux method, brookite and rutile formed in the morphology of agglutinated particles. On the other hand, when the $TiOCl_2$ solution was heated in autoclave, rutile and brookite particles formed separately. The rutile particles had a large size of about $4\,\mu m$, whereas the brookite particles were small in the size of about 100 nm and dispersed in the solution. The rutile and brookite particles were separated by centrifugation. The photocatalytic activity of the brookite particles was investigated on the degradation of methylene-blue in water under UV light irradiation. Compared to commercial brookite particles, the synthesized brookite particles had higher adsorption ability for methylene-blue with the photocatalytic activity. Hydrothermal treatment of synthesized brookite particles was effective for the enhancement of photocatalytic activity because of improvement of crystallinity. In order to enhance the photocatalytic activity, the crystallinity of samples was very important compare to the specific surface area.

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