

# Understanding of Homogeneous Spontaneous Precipitation for Monodispersed TiO<sub>2</sub> Ultrafine Powders with Rutile Phase around Room Temperature

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Monodispersed TiO<sub>2</sub> ultrafine particles were obtained from aqueous TiOCl<sub>2</sub> solution with a 0.67 M Ti<sup>4+</sup> concentration prepared by diluting TiCl<sub>4</sub> with the homogeneous precipitation process in the range 17–230°C. With the spontaneous hydrolysis of TiOCl<sub>2</sub>, which means the natural decrease of the pH value in the aqueous solution, all monodispersed precipitates were crystallized with the anatase or rutile TiO<sub>2</sub> phase during the reactions. The TiO<sub>2</sub> precipitate with the pure rutile phase was fully formed at temperatures below 65°C, which did not involve the evaporation of H<sub>2</sub>O, and above 155°C, which were available by suppressing it. The TiO<sub>2</sub> precipitate with the rutile phase, including a small amount of the anatase phase, started to be formed at intermediate temperatures above 70°C, showing the full formation of the anatase phase above 95°C under the free evaporation of H<sub>2</sub>O. However, in the case of completely suppressing H<sub>2</sub>O evaporation at temperatures above 70°C, the TiO<sub>2</sub> precipitate with the anatase phase that had already been formed by rapid reaction was fully transformed with the reaction time into the precipitate with the rutile phase by the vapor pressure of H<sub>2</sub>O. Therefore, the formation of TiO<sub>2</sub> precipitates with the rutile phase around room temperature would be caused by the existence of capillary pressure between the agglomerated needle-shaped particles or the ultrafine clusters, together with the slow reaction rate. © 1999 Academic Press

## 1. INTRODUCTION

TiO<sub>2</sub> with rutile phase has been widely used as a white pigment material because of an excellent light-scattering effect along with a coating material for optical or electronic devices because of its high dielectric constant, high refractive index, and chemical stability, even in strongly acidic or basic environments (1–4). TiO<sub>2</sub> with rutile phase for applications in optical or electronic devices has generally been adopted in the form of a thin film using various fabrication

methods such as rf sputtering, e-gun evaporation, chemical vapor deposition, and sol–gel. However, these methods resulted in a thin film of TiO<sub>2</sub> with the substoichiometry or amorphous phase. Thus, it is necessary to dope other elements during the deposition of the film for the stability of the anatase phase or to anneal it for the conversion of anatase to rutile phase at temperatures above 400°C for long times. On the other hand, the screen-printing or casting method with the nanosized rutile TiO<sub>2</sub> powders has recently received the attention of the direct application for the dielectric layer of an ac powder electroluminescent device in place of the heat treatment of the thin film prepared using various vacuum techniques (5). In this method, the nanosized rutile TiO<sub>2</sub> ultrafine powders mixed with binder are casted or screen-printed on the substrate and are then cured at temperatures below 200°C for the removal of the binder. Afterward, a special encapsulation process of the casted or screen-printed layer is carried out for direct application, which will be a very economical process for optical or electronic devices. For this process, first of all, the ultrafine TiO<sub>2</sub> homogeneous powder with rutile phase should be more massively produced than that with anatase phase.

Up to now, the various processes such as the sulfate, the chloride, the hydrothermal, and the sol–gel processes for the fabrication of TiO<sub>2</sub> powder with the rutile phase have been developed (6–10). To prepare the rutile TiO<sub>2</sub> ultrafine powder using one of the above processes, however, many faults, such as high costs for high temperatures of synthesis and heat treatment, difficulties in continuous process, low efficiencies in production, and contamination of impurities during the crushing or pulverizing, should be overcome. Kim *et al.* recently developed a very economical process for ultrafine TiO<sub>2</sub> homogeneous powder with rutile phase just by heating an aqueous TiOCl<sub>2</sub> solution from TiCl<sub>4</sub>, which enhances the spontaneous precipitation of TiO<sub>2</sub> (11, 12). With simple dilution and heating of a highly viscous TiOCl<sub>2</sub> solution obtained from the reaction between water and TiCl<sub>4</sub> at temperatures below 100°C, the monodispersed

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crystalline TiO<sub>2</sub> powder with specific surface areas of about 150 m<sup>2</sup>/g was easily obtained with efficiencies above 85% in production. Moreover, it was highly evaluated for the applications because the ultrafine TiO<sub>2</sub> powder with rutile phase, formed thermodynamically at temperatures higher than 600°C, was obtained even around room temperature. In their process the reverse phase transition of rutile to anatase phase with an increase in the reaction temperature was also found to occur because of the difference in the reaction rate of the precipitation of the ultrafine TiO<sub>2</sub> powder. However, it could not yet be appropriately explained because of the absence of many experimental data, except for the reaction rate in their paper.

Therefore, there is ample interest in closely examining the homogeneous precipitation mechanism of crystalline TiO<sub>2</sub> ultrafine powder in aqueous TiOCl<sub>2</sub> solution. The object of this paper, for the extension of the development for a new synthesis method of the ultrafine TiO<sub>2</sub> powder, is to investigate in detail the reaction of TiOCl<sub>2</sub> with H<sub>2</sub>O for the homogeneous precipitation. Thus, the shapes and the changes in the crystalline state of the TiO<sub>2</sub> precipitates under various precipitation conditions were observed to find the precipitation mechanism of ultrafine TiO<sub>2</sub> powder from aqueous TiOCl<sub>2</sub> solution.

## 2. EXPERIMENTAL PROCEDURE

Transparent titanium tetrachloride (TiCl<sub>4</sub>, 3 N, Aldrich Co.) was used as a starting material to fabricate the ultrafine TiO<sub>2</sub> powder using the homogeneous precipitation method. First, to prepare aqueous TiOCl<sub>2</sub> solution with a high viscosity to use as a stock solution, TiCl<sub>4</sub>, which had been cooled below 0°C, was put into a constant temperature (0°C) reaction container, and then distilled water ice pieces were slowly added to the container for a hydrolysis reaction. During the reaction, yellow cakes, such as an unstable TiO(OH)<sub>2</sub> intermediate product, were formed at first together with the slow melting of ice pieces and then they dissolved with the continuously added ice pieces to form a yellow aqueous TiOCl<sub>2</sub> solution with a Ti<sup>4+</sup> ion concentration of 4.7 M. Finally, distilled water was added to this stock solution to obtain a transparent aqueous TiOCl<sub>2</sub> solution with a Ti<sup>4+</sup> concentration of 0.67 M for the homogeneous precipitation. For the precipitation of TiO<sub>2</sub> from aqueous TiOCl<sub>2</sub> solution, a cylindrical reservoir (inner diameter 80 mm × length 100 mm × thickness 6 mm) obtained by machining the Teflon rod was utilized to completely seal itself using a cover with a Viton O-ring in the water bath or oven during the reaction at 17–230°C. Also, for the safety of experiments, the mini autoclave of the SS316 with Teflon lining was used because the precipitation reactions above 160°C were performed under the pressures above 5 bar of water vapor.

After the precipitation was complete and it was left untouched for 24 h, the precipitates were filtered using distilled water or ethyl alcohol and a PTFE membrane filter (Micro-Filtration System Co.) with a porosity of 0.1 μm to completely remove Cl<sup>-</sup> ions from the precipitates. The filtered precipitates were dried at 150°C for 12 h to obtain the final powder. All of the chemical agents used in this study have analytical reagent grades. The pH values of aqueous TiOCl<sub>2</sub> solution during the precipitation were measured using a 355 ion analyzer (Mettler Toledo Co.). The crystallinities of the dried precipitates were analyzed using XRD (Rigaku D/Max-IIIc: 3 kW/40 kV, 45 mA) with CuKα radiation and TEM diffraction, and the shape of the precipitates was examined by SEM (JEOL ABT DX-130S: 3 kV). Also, the specific surface area of the precipitate was measured by the BET method after drying at 200°C for 24 h. The efficiencies of the precipitates in production were calculated by weighing the precipitates after the heat treatment at 1000°C for 60 min or by analyzing the concentration of Ti<sup>4+</sup> ions remaining in the aqueous TiOCl<sub>2</sub> solution using ICP-AES after the filtration.

## 3. RESULTS AND DISCUSSION

Originally transparent TiCl<sub>4</sub> solution is a material which has a large vapor pressure at room temperature and hydrolyzes readily by reacting with water from the air. When a substoichiometric amount of H<sub>2</sub>O is added to transparent TiCl<sub>4</sub>, it was found that the hard, yellow hydroxide material first formed was easily dissolved in strongly acidic HCl solution and then finally *in situ* converted to an aqueous TiOCl<sub>2</sub> solution of yellow color. Moreover, homogeneous precipitation occurred in that solution by a simple heating method (11, 12). In the preparation process of the aqueous TiOCl<sub>2</sub> solution, the solution was simultaneously prepared with a self-generating HCl solution by the dissociation of TiCl<sub>4</sub> into yellow hydroxide and HCl under the conditions of the addition of a substoichiometric amount of H<sub>2</sub>O to TiCl<sub>4</sub>.

First of all, to compare the precipitation behavior in aqueous TiOCl<sub>2</sub> solutions with various concentrations of Ti<sup>4+</sup>, the precipitates were prepared using a simple heating method in the closed reaction reservoir made of Teflon. Figure 1 shows SEM photographs for the powders obtained from the precipitation in aqueous TiOCl<sub>2</sub> solutions with 4.7 and 0.67 M Ti<sup>4+</sup> concentrations by a simple heating method at 140°C for 60 min. All the precipitates were with the rutile phase of TiO<sub>2</sub>. Largely elongated particles with sizes ranging from 60 to 100 μm due to the severe agglomerations of the small precipitates are formed in the case of a higher concentration of Ti<sup>4+</sup>. However, in the case of a lower concentration of Ti<sup>4+</sup> by the large addition of H<sub>2</sub>O to aqueous TiOCl<sub>2</sub> solution with a Ti<sup>4+</sup> concentration of 4.7 M, the obtained precipitates are very fine and

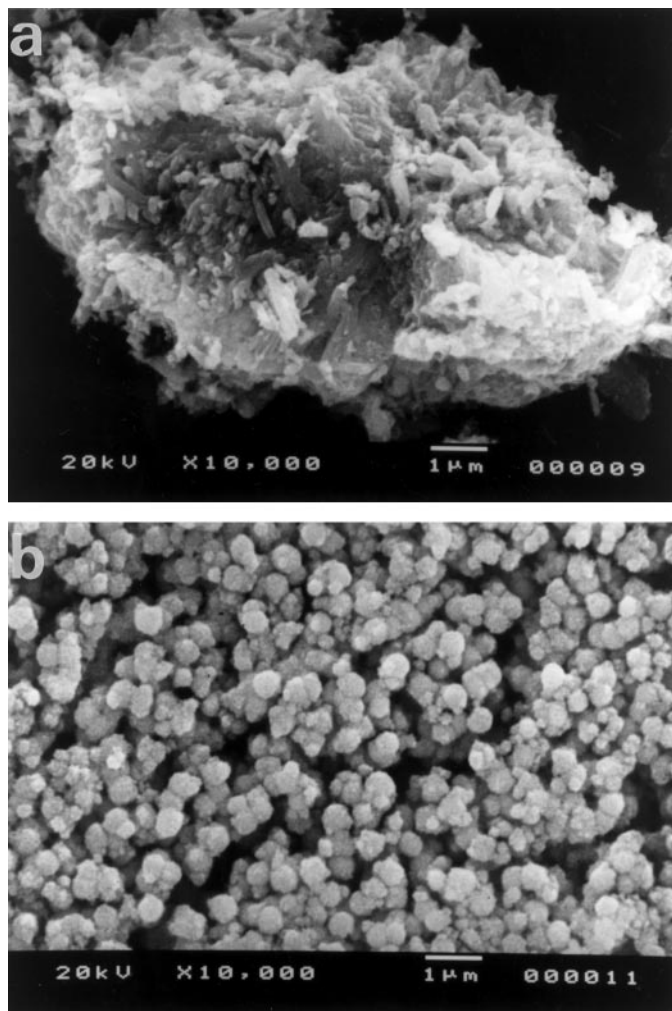


FIG. 1. SEM photographs for the crystalline  $\text{TiO}_2$  powders prepared from (A) 4.7 M and (B) 0.67 M  $\text{Ti}^{4+}$  aqueous solutions at  $140^\circ\text{C}$  for 60 min.

monodispersed with sizes of 0.2–0.4  $\mu\text{m}$  (specific surface areas of about  $179 \text{ m}^2/\text{g}$ ). On the other hand, no precipitates were observed when the original  $\text{TiCl}_4$  solution was heated without the addition of  $\text{H}_2\text{O}$  under the same conditions. The productive efficiency for  $\text{TiO}_2$  powders from aqueous  $\text{TiOCl}_2$  solution with the increases in the amount of  $\text{H}_2\text{O}$  added at the reaction temperature of  $50^\circ\text{C}$  increases up to more than 85% at 90 vol%  $\text{H}_2\text{O}$  and then became about 90% at more than those amounts, as shown in Table 1. Therefore, these indicate that the addition of  $\text{H}_2\text{O}$  alone to make  $\text{TiCl}_4$  or  $\text{TiOCl}_2$  dilute for the reaction can control the shapes and amounts of the precipitates even if none of the special additives containing important elements such as  $\text{O}^{2-}$  or  $\text{OH}^-$  are furnished to form the crystalline precipitates of  $\text{TiO}_2$ .

Figure 2 shows the productive efficiencies for the powders that were precipitated for 4 h with extra additions of various

TABLE 1  
Productive Efficiency for the Precipitation of  $\text{TiO}_2$  from Aqueous  $\text{TiOCl}_2$  Solution with the Increase in the Amount of Water Added at  $50^\circ\text{C}$

Volume fraction of $\text{H}_2\text{O}$ (%)	Productive efficiency (%)
80.0	0
83.3	0.26
85.9	5.4
89.1	82
90.0	85.9
91.7	89.9
92.9	92.4
94.7	91.5
95.5	92.0

amounts of ethyl alcohol to the  $\text{TiOCl}_2$  solution, including the same amount of  $\text{H}_2\text{O}$  during the same reaction time. After the precipitation, the precipitates were filtered using the paper with a porosity of 0.1  $\mu\text{m}$  and then were dried at  $150^\circ\text{C}$  for 12 h in open air. As the amount of the added ethyl alcohol increases, the productive efficiency of the precipitated powders decreases dramatically. It was, however, confirmed that, with showing almost the same efficiencies at the reaction times more than 24 h in this figure, the concentration of  $\text{Ti}^{4+}$  remaining in the aqueous  $\text{TiOCl}_2$  solution after filtration was almost the same, as low as 10 wt%, regardless of the amount of added ethyl alcohol according to the result of ICP-AES analysis. It was also confirmed that because the

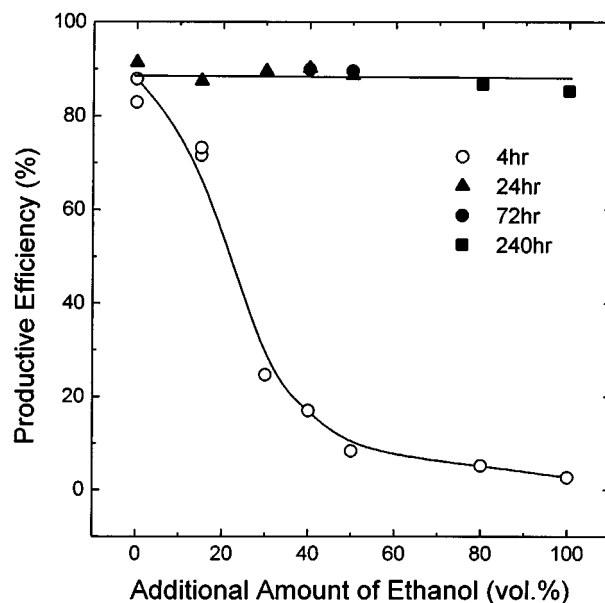
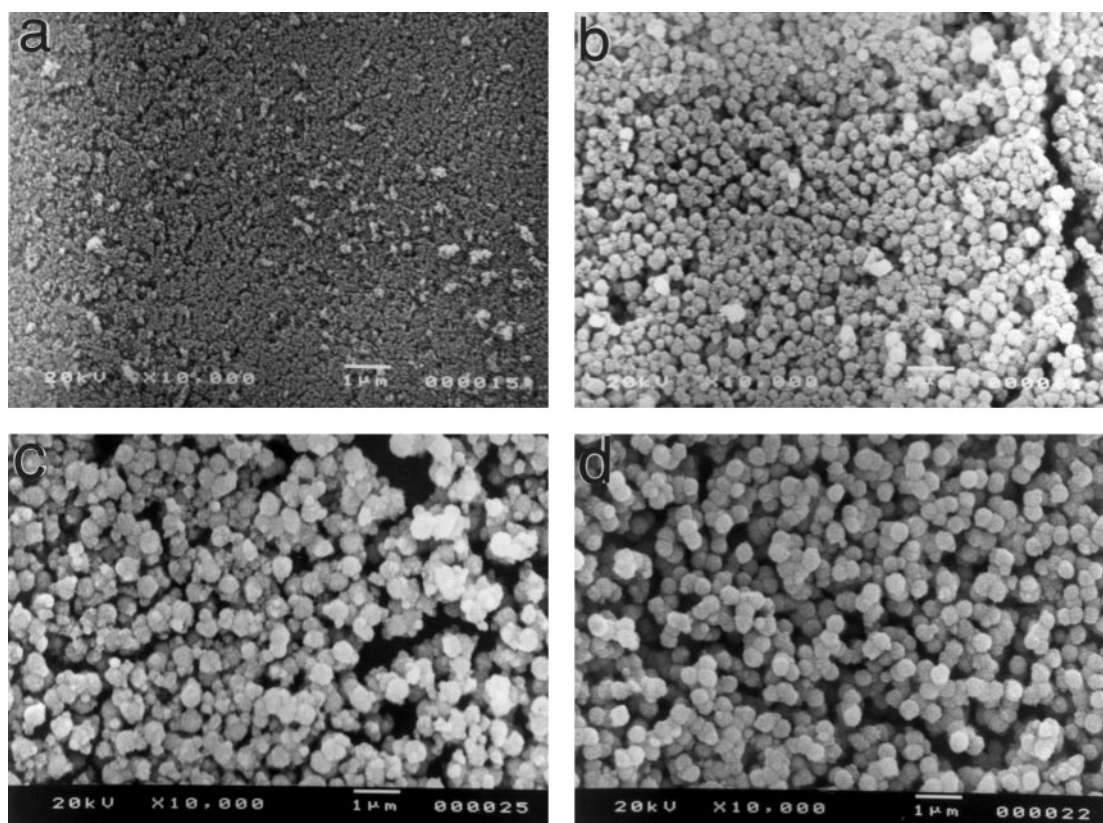


FIG. 2. The productive efficiency for the crystalline  $\text{TiO}_2$  powders prepared from 0.67 M  $\text{Ti}^{4+}$  aqueous solution with the various additional amounts of ethanol.



**FIG. 3.** SEM photographs for the crystalline TiO<sub>2</sub> powders prepared from 0.67 M Ti<sup>4+</sup> aqueous solution under the reaction conditions of (A) 17°C for 7 days, (B) 60°C for 4 h, (C) 100°C for 2 h, and (D) 150°C for 1 h.

precipitates formed together with the addition of ethyl alcohol were very ultrafine or not formed, compared to the case of no addition of ethyl alcohol, they mostly passed through the filtering paper in the case of the short time reaction condition. On the other hand, it was found from many preliminary experiments that the ethyl alcohol did not take part in the reaction and did not provide OH<sup>-</sup> ions for the hydrolysis of TiOCl<sub>2</sub>. Thus, it can be assumed that the site number for the nucleation of TiO<sub>2</sub> in the solution is the same as the amount of H<sub>2</sub>O supplied, regardless of the various amounts of ethyl alcohol. Therefore, it can be said that the decrease of the efficiency in production would be due to the slow growth rate of the precipitates by the screening effect of ethyl alcohol based on the real decrease in the volume fraction of the amount of H<sub>2</sub>O surrounding the TiOCl<sub>2</sub> molecules. Conclusively, it is suggested that the precipitation of TiO<sub>2</sub> ultrafine particles in aqueous TiOCl<sub>2</sub> solution occurs easily and rapidly when the sufficient amounts of H<sub>2</sub>O are supplied.

The precipitation of TiO<sub>2</sub> was carried out in aqueous TiOCl<sub>2</sub> solution with a 0.67 M Ti<sup>4+</sup> concentration under the reaction conditions with the same efficiency in production and then the shape of the precipitate was observed, as shown in the SEM photographs of Fig. 3. It was confirmed

that longer times were necessary to obtain the same productive efficiency at lower temperatures due to the smaller reaction rate in the solution. Monodispersed precipitates are formed, having increasing spherical sizes in the range of 40–400 nm with the reaction temperatures. As shown in Fig. 4, with respect to the XRD results, the precipitates consist of the completely rutile phase of TiO<sub>2</sub> at 17, 60, and 150°C and consist of the rutile phase including a small amount of the anatase phase of TiO<sub>2</sub> at 100°C alone. On the other hand, it was observed that the crystalline structure of the dried precipitates was not changed with the annealing temperatures below 400°C, regardless of long annealing time in air. Generally, the anatase phase of TiO<sub>2</sub>, formed thermodynamically at low temperatures, is obtained around 400°C by the transformation from the amorphous phase formed at lower temperatures. Therefore, it can be known that all our precipitates were crystallized with the stable structures at temperatures lower than 150°C, even at room temperature. It was reported that TiO<sub>2</sub>, in the general synthesis of TiO<sub>2</sub> using the alkoxide, existed with the amorphous phase at temperatures lower than 400°C and the anatase phase at lower temperatures than 650°C and then transformed to the rutile phase at higher temperatures (10). However, it was reported by Kim *et al.* that using aqueous

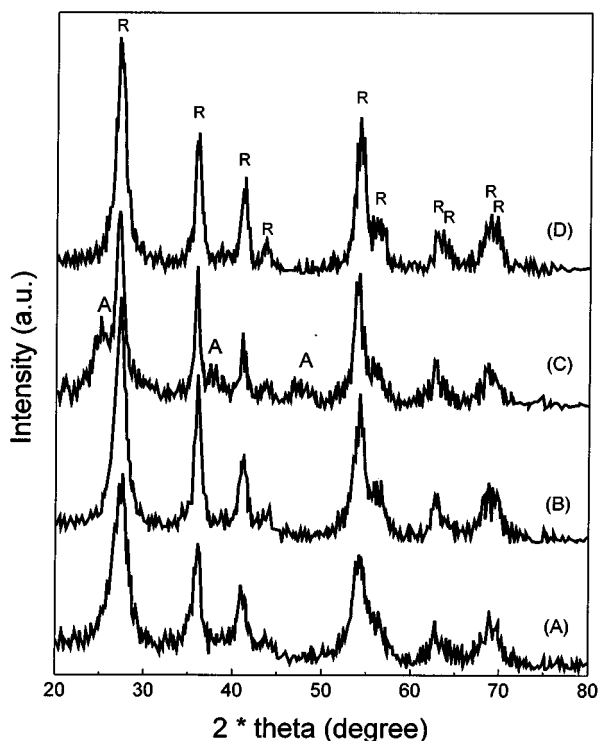


FIG. 4. XRD patterns for the  $\text{TiO}_2$  powders shown in Fig. 1. (R, rutile; A, anatase).

$\text{TiOCl}_2$  solution under the condition of free evaporation of  $\text{H}_2\text{O}$  during the reaction formed the rutile phase of  $\text{TiO}_2$  because of the slow reaction rate for the precipitation below  $65^\circ\text{C}$ , and a small amount of the anatase phase started to form at higher temperatures. Then, the complete anatase phase formed due to the rapid reaction rate at  $100^\circ\text{C}$  (11, 12). On the other hand, it can be seen that most of the precipitates consist of the rutile phase alone if the free evaporation of  $\text{H}_2\text{O}$  was suppressed at temperatures even higher than  $70^\circ\text{C}$ , as shown in Figs. 3C and 3D.

In the dilute  $\text{TiOCl}_2$  solution obtained from  $\text{TiCl}_4$ , crystalline  $\text{TiO}_2$  particles were directly precipitated and at that time their structure was also purely rutile at the lower as well as the higher reaction temperatures, except for the intermediate temperatures at around  $100^\circ\text{C}$ . Various experiments were made to investigate these reasons. At first, to confirm how the direct precipitation of  $\text{TiO}_2$  from aqueous  $\text{TiOCl}_2$  solution occurred, pH value changes of aqueous  $\text{TiOCl}_2$  solution with the reaction time were measured below  $80^\circ\text{C}$ , as shown in Fig. 5. Here, the pH value was not measured above  $80^\circ\text{C}$  due to boiling of the solution. At the same concentration of  $\text{Ti}^{4+}$ , as the reaction temperature increases, despite the pH value becoming relatively higher by the temperature effect, the pH values are almost constant or show little decrease at the early stage and then great decrease after some time. This abrupt decrease in the pH

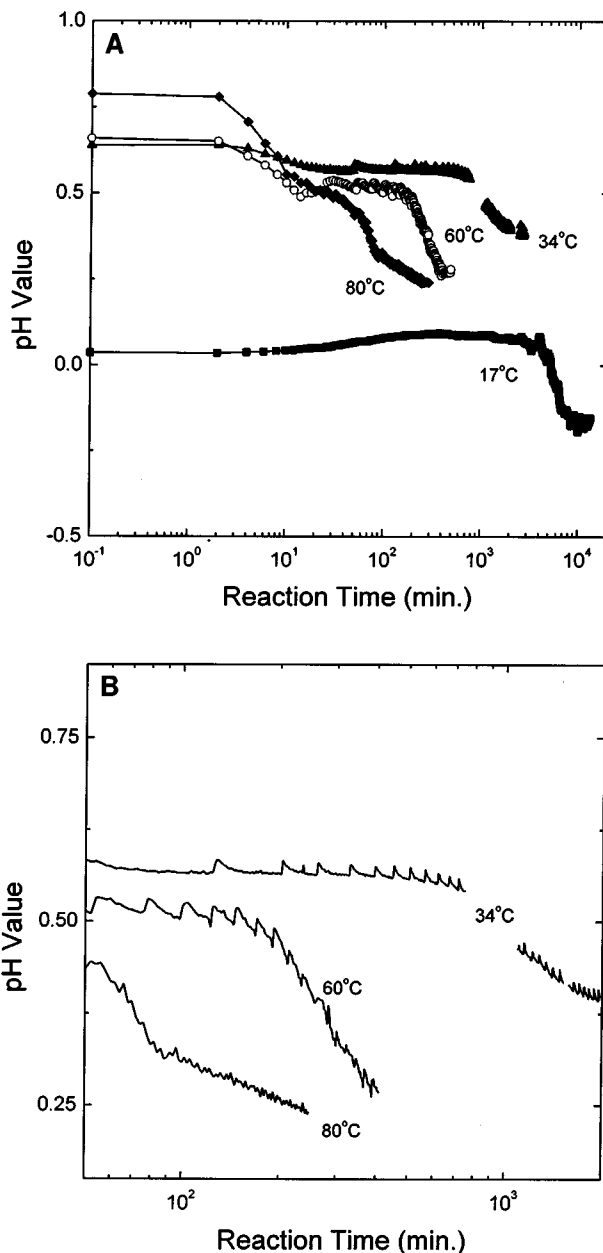
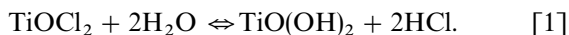


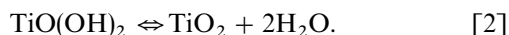
FIG. 5. The pH value changes of  $0.67 \text{ M Ti}^{4+}$  aqueous solution with the reaction time at various temperatures, where Fig. 5B is an enlarged part of Fig. 5A.

value with time agreed with the starting of the large precipitation in the aqueous  $\text{TiOCl}_2$  solution. This also occurs at a faster rate with a greater increase in the reaction temperature. In other words, a higher reaction temperature enhances the large precipitation in a shorter time. Thus, it can be known that the precipitation of  $\text{TiO}_2$  with the reaction time resulted in the decrease of the  $\text{OH}^-$  ion concentration or the increase of the  $\text{H}^+$  ion concentration in aqueous  $\text{TiOCl}_2$  solution from the measurement of the decrease in the pH

value. Therefore, irrespective of the reaction temperatures, the entire precipitation reaction occurred accompanied by the hydrolysis of TiOCl<sub>2</sub> like the reaction in Eq. [1] via the formation of an intermediate hydroxide:



Also, as shown in Fig. 5B as an enlarged part of Fig. 5A, it is observed that a repeatedly small increase and decrease in the pH value of a shape such as sawtooth is displayed continuously during the decrease in the pH value over the entire reaction time. Because this was repeatedly measured in all the conditions, the local variations in the pH value of the solution like this phenomenon may indicate the release of H<sub>2</sub>O from TiO(OH)<sub>2</sub> during the crystallization or precipitation, as shown in the reaction in Eq. [2]:



Therefore, it can be suggested that the synthesis of crystalline TiO<sub>2</sub> by the reaction of H<sub>2</sub>O with TiOCl<sub>2</sub> occurred by the precipitation with hydrolysis, together with the crystallization. On the other hand, the driving force for this spontaneous formation of crystalline TiO<sub>2</sub> from the aqueous TiOCl<sub>2</sub> solution even at room temperature may be ascribed to the instability of TiOCl<sub>2</sub> in the aqueous solution. Namely, when a TiOCl<sub>2</sub> molecule is dispersed to be encircled with many H<sub>2</sub>O molecules in the solution, the hydrolysis of TiOCl<sub>2</sub> is more enhanced compared to the TiOCl<sub>2</sub> molecule exposed to the air or to substituted ethyl alcohol solution partially in place of H<sub>2</sub>O. On the other hand, in the case of the partial addition of ethyl alcohol instead of H<sub>2</sub>O or the extra addition of ethyl alcohol to the same voluminous TiOCl<sub>2</sub> solution, there was a smaller decrease of the pH value, a larger decrease of the productive efficiency, and a slower reaction rate than in a normal aqueous TiOCl<sub>2</sub> solution. Thus, it can be thought from both the previous reports (11, 12) and Fig. 2 that this was because the ethyl alcohol, on behalf of the H<sub>2</sub>O molecules surrounding the TiOCl<sub>2</sub> molecules, actually reduced the number of OH<sup>-</sup> ions supplied for TiOCl<sub>2</sub> by the H<sub>2</sub>O molecules.

In Fig. 3, all the TiO<sub>2</sub> precipitates from the reaction of H<sub>2</sub>O with TiOCl<sub>2</sub> were crystalline, not amorphous. They were pure rutile phase at all the reaction temperatures except for the mixture of the rutile and anatase phases at 100°C alone. During the precipitation reaction, to investigate how the crystalline status of TiO<sub>2</sub> was determined, all the TiO<sub>2</sub> powders formed at the ranges of 17–230°C were characterized using XRD and SEM. Because the formed precipitates always consisted of rutile and/or anatase phases of TiO<sub>2</sub> in this experiment, the volume fraction of the rutile phase of TiO<sub>2</sub> prepared under various conditions was calculated using K.-N. P. Kumar's equation [13] after the measurement of XRD and the results are shown in Fig. 6.

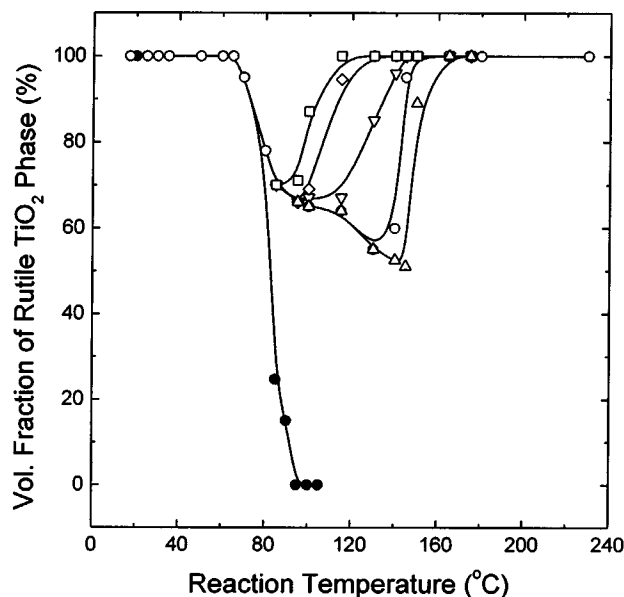
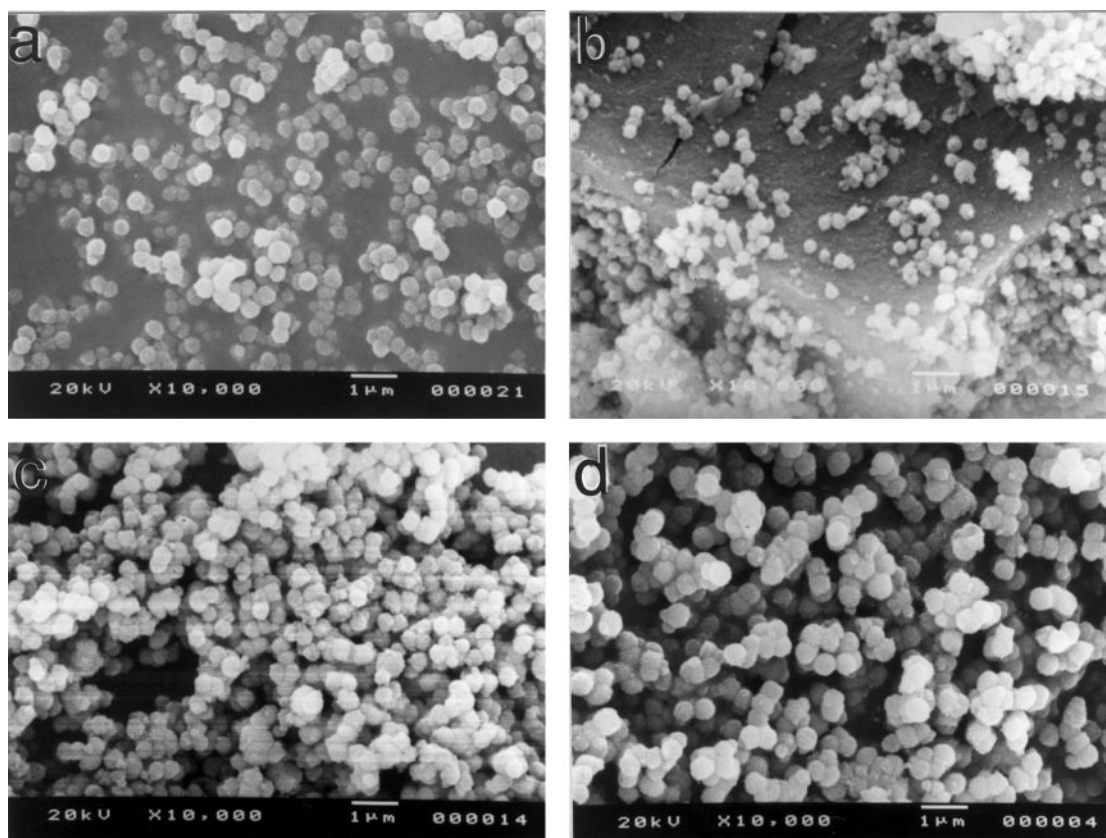


FIG. 6. The volume fraction of rutile TiO<sub>2</sub> phase formed with the various reaction times. (closed data, —●— 300 min under free evaporation of H<sub>2</sub>O; open data, 300 min at the temperatures below 65°C; —△— 20 min, —○— 30 min, —▽— 40 min, —◇— 60 min, and —□— 120 min at the temperatures above 70°C under no evaporation of H<sub>2</sub>O).

Here, the rutile phase of TiO<sub>2</sub> alone is always formed regardless of the various reaction times in the temperatures below 65°C as well as above 155°C. However, in temperatures of 70–150°C, the anatase phase of TiO<sub>2</sub> is mainly formed under the free evaporation of H<sub>2</sub>O in the reaction reservoir, whereas under the conditions to prevent H<sub>2</sub>O evaporation completely, the rutile phase of TiO<sub>2</sub>, including a small amount of the anatase phase, is formed. In this range, the amount of the anatase phase increases with the increase in the reaction temperature for increasingly shorter reaction times and the amount of the rutile phase increases for increasingly longer reaction times. As reported previously (11, 12), the increase in the amount of the anatase phase above 70°C may have occurred by the easy formation of the anatase phase due to the rapid rate of the precipitation reaction. However, it is not explained by the reaction rate that, at the same temperature, the anatase phase of TiO<sub>2</sub> was transformed into the rutile phase with an increasing reaction time. Figure 7 shows the SEM photographs for the powders prepared with the reaction time. As the reaction time increases, the size of the monodispersed particles increases somewhat, not showing the changes of the shape. Here, because the precipitates at 85°C for 120 min consisted of a rutile phase including an anatase phase and those at 115°C for 60 min consisted of a pure rutile phase, the observation of microstructures like these cannot explain the mechanism for the precipitation reaction appropriately.

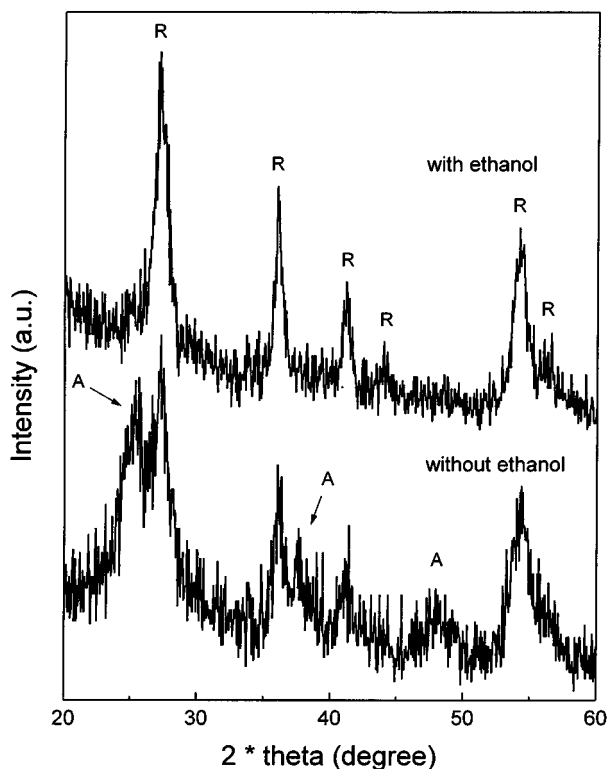
On the other hand, the formation of the rutile phase of about 65 vol% was observed in the reaction at 115°C for



**FIG. 7.** The SEM photographs for the crystalline  $\text{TiO}_2$  powders prepared from 0.67 M  $\text{Ti}^{4+}$  aqueous solution under the reaction conditions of (A) 85°C for 120 min, (B) 115°C for 20 min, (C) 115°C for 60 min, and (D) 115°C for 180 min.

40 min under the condition to prevent the evaporation of  $\text{H}_2\text{O}$  completely. However, the formation of the rutile phase of 100 vol% is observed under the same conditions by the extra addition of ethyl alcohol to the reaction reservoir, as shown in the XRD results of Fig. 8. However, when the ethyl alcohol was added to the reaction solution, the anatase phase still existed in times shorter than 40 min. It was also confirmed that the anatase phase was almost transformed into the rutile phase if the precipitates were filtered after applying a pressure of more than 4 bar for 24 h. These mean that the crystalline structure of the  $\text{TiO}_2$  precipitate during the reaction could be affected by applying a large internal pressure by the vapor pressures of  $\text{H}_2\text{O}$  and ethyl alcohol in the reservoir. Therefore, it is possible to make out that the rutile phase of  $\text{TiO}_2$  precipitates above 70°C was transformed from the anatase phase, which had been formed first because the internal pressure in the reaction reservoir applied or increased at higher temperatures. In other words, it can be thought that the higher internal pressure by the vapor pressure of  $\text{H}_2\text{O}$  at the higher reaction temperature causes the already formed anatase phase to transform into the rutile phase.

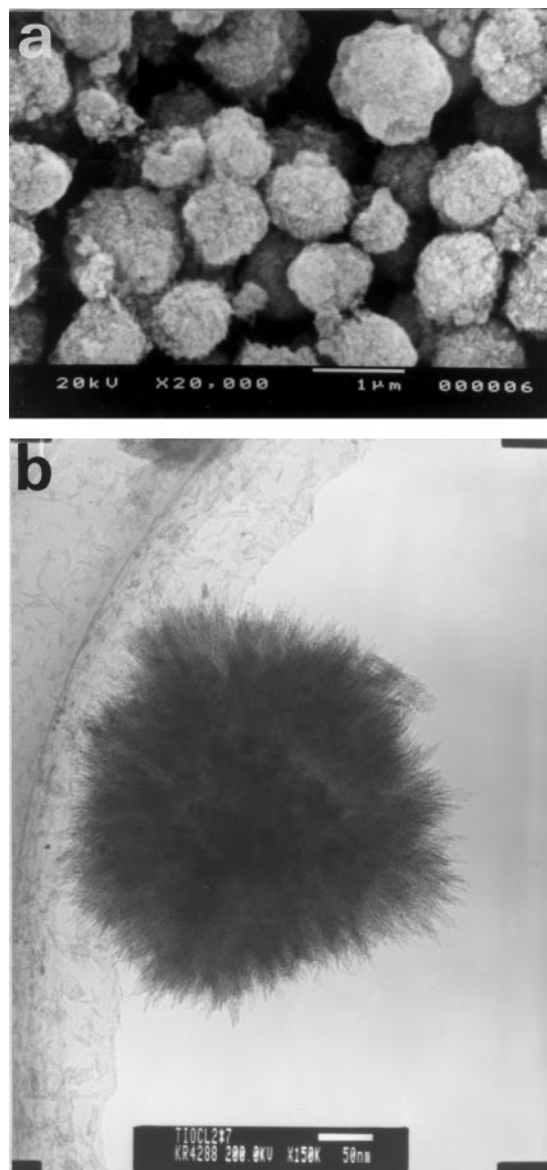
However, as shown in Fig. 6, all the  $\text{TiO}_2$  precipitates consisted of the rutile phase alone, regardless of the various reaction temperatures below 65°C, and the precipitates obtained in a short time were also the rutile phase showing a weak crystalline state, not the anatase or amorphous phase. Therefore, the fact that although below 65°C not only was the reaction rate very low but also the internal pressure by the reaction reservoir was almost not applied, the pure rutile phase was more easily formed compared to the conditions at the high reaction temperature is not understood. In accordance with Zhang and Banfield's simulated results (14), they showed that the anatase phase of  $\text{TiO}_2$  is more stable thermodynamically with the decrease in size of a  $\text{TiO}_2$  particle. They also insisted that to form the rutile phase of  $\text{TiO}_2$ , the size of the particle should be more than about 8 nm, not considering the surface stress, whereas more than about 14 nm considering the surface stress. However, with respect to our XRD and TEM measurements, the size of the primary particles for the rutile phase of  $\text{TiO}_2$  was in the range of 3–10 nm by the homogeneous spontaneous precipitation method. Thus, their results are not applied to our conditions because our values were smaller than those



**FIG. 8.** The XRD patterns for the crystalline TiO<sub>2</sub> powders prepared for 0.67 M Ti<sup>4+</sup> aqueous solution with and without the addition of ethanol under the reaction conditions of 115°C for 40 min.

of the anatase phase for the primary particle. On the other hand, Hwang *et al.* explained that the capillary pressure between charged clusters played an important role in the synthesis of a diamond, which theoretically requires high temperature and pressure conditions, using the CVD method (15–18). They suggested that diamond thin film in place of graphite thin film from a carbon source during the CVD process was easily formed because of the capillary pressure that existed between the ultrafine charged clusters in the gas phase. Also, Multani's group in India (19–21) reported that as the primary particles of PbTiO<sub>3</sub>, BaTiO<sub>3</sub>, CeO<sub>2</sub>, CuO, and Al<sub>2</sub>O<sub>3</sub> powders decreased with smaller sizes, their crystalline structure transformed with a symmetry of nearly  $c/a = 1$  by the increase in the capillary pressure in the agglomerated powders. Here,  $a$  and  $c$  mean the lattice parameters in the  $x$  and  $z$  axis, respectively. Figure 9 shows the SEM and TEM photographs for the particles ( $\sim 1$  and  $\sim 0.3$   $\mu\text{m}$ ) of the rutile phase precipitated at 50°C using ultrasonic stirring and magnetic stirring methods, respectively. That a particle consists of many fine particles, not a primary particle (Fig. 9A), on the surface of the particle, and the particle also consists of many fine acicular or needle-shaped particles, as shown at the edge of the particle is observed (Fig. 9B). Thus, it can be thought

that the precipitation of a crystalline TiO<sub>2</sub> particle from aqueous TiOCl<sub>2</sub> solution was carried out together with the agglomeration of fine clusters or fine acicular-shaped particles. Also, the rutile phase of TiO<sub>2</sub> is more symmetric crystallographically than the anatase phase. It can be thought from these results, therefore, that at lower reaction temperatures the capillary pressure (negative pressure) formed between the clusters or the fine particles would easily enhance the formation of the rutile phase more symmetrically than the anatase phase.



**FIG. 9.** The SEM and TEM photographs for the representative rutile TiO<sub>2</sub> powders from 0.67 M Ti<sup>4+</sup> aqueous solution: (A) by ultrasonically stirring at 50°C and (B) by normally stirring at 50°C.



#### 4. CONCLUSIONS

The monodispersed TiO<sub>2</sub> ultrafine particles with diameters of 40–400 nm were obtained from aqueous TiOCl<sub>2</sub> solution with a 0.67 M Ti<sup>4+</sup> concentration prepared by diluting TiCl<sub>4</sub> with the homogeneous spontaneous precipitation process. The process was carried out under conditions to prevent H<sub>2</sub>O evaporation completely in the range of 100–230°C and to make it freely or to prevent it thoroughly in the range of 17–100°C. The results are as follows.

The precipitation of TiO<sub>2</sub> ultrafine particles by the reaction of TiOCl<sub>2</sub> with H<sub>2</sub>O occurred easily and rapidly when sufficient amounts of H<sub>2</sub>O were supplied. With the spontaneous hydrolysis of TiOCl<sub>2</sub>, which means the natural decrease in the pH value of the aqueous TiOCl<sub>2</sub> solutions, all the monodispersed precipitates were crystallized with the anatase or rutile TiO<sub>2</sub> phase during the reaction regardless of various conditions. The TiO<sub>2</sub> precipitate with a pure rutile phase was fully formed at temperatures below 65°C, which did not involve the evaporation of H<sub>2</sub>O, and above 155°C, which were available by suppressing it. The TiO<sub>2</sub> precipitate with the rutile phase, including a small amount of the anatase phase, started to be formed in the intermediate temperatures above 70°C and showed the full formation of anatase above 95°C under the free evaporation of H<sub>2</sub>O. However, in the case of completely suppressing H<sub>2</sub>O evaporation at temperatures above 70°C, the TiO<sub>2</sub> precipitate with the anatase phase that had already been formed by rapid reaction was fully transformed with the reaction time into the precipitate with the rutile phase by the vapor pressure of H<sub>2</sub>O. Therefore, it can be thought that these crystallization behaviors of TiO<sub>2</sub> precipitates such as the formation of the rutile phase around room temperature would be caused by the existence of capillary pressure between the agglomerated needle-shaped particles or the ultrafine clusters, together with the slow reaction rate.

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