Effect of HCl concentration and reaction time on the change in the crystalline state of TiO_2 prepared from aqueous $TiCl_4$ solution by precipitation

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Abstract

TiO_2 powder with 50% by volume or more of brookite phase was obtained by heating aqueous $TiCl_4$ solution, whose final concentration of HCl after reaction was kept between 4.9 and 6.4 M, at 80 °C for 15 h. Rutile-type TiO_2 was obtained at 5 h of reaction time, a mixture of predominant brookite and rutile at 10–15 h while rutile phase was formed at 25 h. Brookite phase was transformed directly to rutile phase with increase of reaction time but to rutile via anatase phase through heat treatment.
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Keywords: $TiCl_4$; TiO_2; Brookite; Precipitation; HCl

1. Introduction

Nanocrystalline materials, which are composed of ultra-fine crystals with dimensions from several to tens of nanometers, have received increasing attention in various fields by virtue of their special chemical, physical and mechanical properties.[1–3] Of these materials titanium dioxide is largely used in technical application.[1–4] Natural polymorphs of TiO_2 are known to exist as tetragonal rutile and anatase and orthorhombic brookite.[1–6] Generally, titanium oxide is obtained either from minerals or from a solution of titanium salts or alkoxides through one of the various processes such as the sulfate, the chloride, the hydrothermal method, and the sol–gel process.[3–6] Rutile phase is used as a white pigment, a coating material for optical lenses and a dielectric material because of its high refractive index compared to other materials.[3–9] Anatase-type TiO_2 is used as a photocatalyst in environmental purification and optical electrochemical applications. Anatase and rutile phases, therefore, are well known

and many studies on their synthesis, photocatalysis and application for catalyst supports have been reported. But, few studies on the synthesis of brookite-type TiO_2 or its application have been reported.[2,10–14] Pottier et al.[2] reported that TiO_2 with the brookite structure could be formed by thermolysis of $TiCl_4$ in HCl medium. In this report, they insisted that the chloride ions in the precipitation medium allow the formation of brookite and the optimal range of Cl^-_{total} to Ti^{4+} ratio for its formation in aqueous $TiCl_4$ solution is between 17 and 35. Zheng et al.[11,12] have studied the preparation condition that leads to brookite formation by hydrothermal method using titanium compounds, such as $Ti(SO_4)_2$ and $TiCl_4$, as a starting material. Kominami et al.[10] reported that microcrystalline brookite-type TiO_2 without contamination of other TiO_2 phases was formed by use of oxobis(2,4-pentanedionato-O,O')titanium and sodium laurate in organic solvents as the reaction media at higher than their boiling points. Other researchers reported that brookite is sometimes observed as a by-product when the precipitation is carried out in an acidic medium at low temperature.[2,10] Therefore, pure brookite without an admixture of rutile or anatase phase is difficult to prepare and the difficulty in preparing brookite

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having high purity and large surface area is probably one of the reasons for the limited application of brookite-type TiO_2 as a catalyst support and photocatalyst.[10–12]

In this study, $TiCl_4$ was hydrolyzed by HCl solution for preparation of an aqueous $TiCl_4$ stock solution used for synthesis of nanosized crystalline TiO_2 and the stock solution was diluted for precipitation by adding HCl solution with various concentrations. Merely heating the diluted aqueous $TiCl_4$ solution at 80 °C induced precipitation. Thus, the effect of HCl concentration in diluted aqueous $TiCl_4$ solution and reaction time on the changes in the crystalline state of TiO_2 particles and the volume fraction change of crystal structure were examined. Also, structural transformation of TiO_2 particle by heat treatment was estimated at temperatures from 500 to 1100 °C in atmosphere.

2. Experimental

Titanium tetrachloride ($TiCl_4$) with 99.9% purity (Aldrich Chemical Co.) was used as a starting material to prepare the TiO_2 powder using precipitation method. Because $TiCl_4$ generates much heat in hydrolysis it is necessary to properly remove the heat for effective reaction. In order to effectively remove the reaction heat, the reactor for hydrolysis was installed in circulating bath, whose temperature can be controlled below −5 °C by a refrigerator. The hydrolysis reaction was done by adding 1.0 M HCl instead of distilled water dropwise to $TiCl_4$ in reactor. The concentration of titanium in the as-prepared $TiCl_4$ solution was 4.5 M and this was used as a stock solution. Finally, 0.1–8.0 M of HCl was added to this stock solution to obtain a transparent aqueous $TiCl_4$ solution with 0.8 M of Ti^{4+} for precipitation. This aqueous $TiCl_4$ solution was poured into reactor with a lid and placed in the oven at 80 °C by changing the reaction time for precipitation of TiO_2.

After precipitation, the TiO_2 precipitates were filtered, washed with distilled water three times, and separated. Finally, the precipitates were repeatedly cleaned using ethanol until the pH value become neutral, to prevent agglomeration between precipitates. The so-obtained precipitates were dried at 50 °C for 48 h or more to obtain TiO_2 powder. The crystalline structures of the prepared ultrafine-sized particles were analyzed using X-ray diffractometer (Rikagu D/Max *P/N*: 3 kW/40 kV, 45 mA) with Cu Kα ($\lambda = 1.54056$ Å). The shapes of the prepared ultrafine-sized particles were observed using transmission electron microscope (TEM). After drying the TiO_2 powder at 200 °C for 20 h or more, the specific surface area was determined using ASAP 2010 (Micromeritics) according to the BET method. Also, the pH value of aqueous $TiCl_4$ solution during precipitation was measured using a 702 ion analyzer (Orion Co.). The efficiencies of precipitates in production were calculated by analyzing the concentration of Ti^{4+} ions remaining in the aqueous $TiCl_4$ solution using ICP-OES (Perkin-Elmer Optima 3200) after filtration.

3. Results and discussion

Precipitate of TiO_2 was obtained merely by heating the aqueous $TiCl_4$ solution with 0.8 M of Ti^{4+}, which was prepared by adding HCl solution with various concentrations, at 80 °C for 15 h and the XRD patterns of these products are shown in Fig. 1. The product was rutile-type TiO_2 when less than 1.2 or more than 4.0 M of HCl solution was used whereas a mixture of the rutile and brookite was produced at 1.5–3.8 M of HCl solution. With respect to the brookite phase mixed with the rutile phase, because the (1 2 0) diffraction peak ($d = 0.3512$ nm) of the brookite phase overlaps the (1 0 1) diffraction peak ($d = 0.3520$ nm) of the anatase phase at $2\theta = 25.3$, the peaks of areas except for this position were examined in detail to confirm the formation of brookite.[10,13] Then, all the XRD peaks of a mixture were not assigned to anatase structure but brookite and rutile structures. Therefore, it can be said that the crystal structure mixed with the rutile phase is brookite phase. Also, under the condition producing the mixture phase, as the concentration of HCl increases the (1 2 0, 1 2 1) diffraction peaks ($d = 0.3512$ nm, 0.2900 nm) representing brookite phase increased but the (1 1 0) diffraction peak as a main peak of rutile phase decreased, meaning that the volume fraction of brookite phase increased. But, it was not possible to obtain the TiO_2 powders with brookite structure without mixture of rutile or anatase phase in this study. On the other hand, in the case of using 8.0 M HCl, transparent aqueous $TiCl_4$ solution was changed into white opaque solution as the reaction time increased, showing that particles were formed. However, the formed particles were suspended in the solution with a dispersed state without being
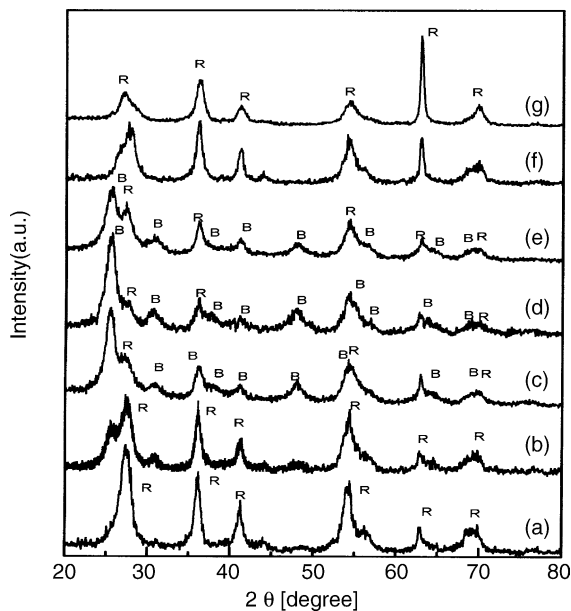

Fig. 1. XRD patterns of TiO_2 particles obtained from aqueous $TiCl_4$ solution with 0.8 M Ti^{4+} prepared by adding 1.2 M (a), 1.5 M (b), 2.5 M (c), 3.5 M (d), 3.8 M (e), 4.0 M (f), and 8.0 M (g) HCl at 80 °C for 15 h (R: rutile; B: brookite).

precipitated. The particles separated by centrifugation of the suspension were rutile phase. From the above results, it can be concluded that the crystal structure formed together with rutile is brookite phase and the HCl solution added to dilute the $TiCl_4$ stock solution is an important factor in determining the crystal structure of TiO_2 precipitate.

Then, supposing that all Ti^{4+} ions in aqueous $TiCl_4$ solution for precipitation converted into TiO_2, an amount of HCl corresponding to four times of the Ti^{4+} concentration is generated as a by-product during oxidation of Ti^{4+} to TiO_2. Therefore, it can be considered that the decisive factor in determining the relative proportion of brookite and rutile structures in TiO_2 precipitate is not the HCl solution added to dilute the $TiCl_4$ stock solution but the final concentration of HCl in the precipitation solution, which is determined by the amount of titanium and that of added HCl for dilution and hydrolysis of $TiCl_4$. In this regard, assuming that complete conversion of Ti^{4+} ions to TiO_2, the final concentrations of HCl at the conditions producing a mixture of brookite and rutile were calculated because the concentration of Ti^{4+} ions remaining in the aqueous $TiCl_4$ solution was negligible after 15 h. Fig. 2 shows the volume fraction of brookite and rutile structures for TiO_2 precipitates as a function of the final concentration of HCl in aqueous $TiCl_4$ solution after reaction. Here, the volume fractions of brookite and rutile structures were calculated by the K.N.P. Kumar equation using intensities of the (1 1 0) main peak of rutile phase and the (1 2 0) main peak of brookite phase in Fig. 1. As shown in Fig. 2, when the final concentration of HCl was kept in the range of 4.5–6.5 M a mixture of brookite and rutile phases was obtained and the volume fraction of brookite phase at near 6.1 M obtained by adding 3.5 M HCl to the aqueous $TiCl_4$ stock solution was maximum value of about 85% but reduced to about 65% at near 6.4 M, disappeared to yield only rutile at
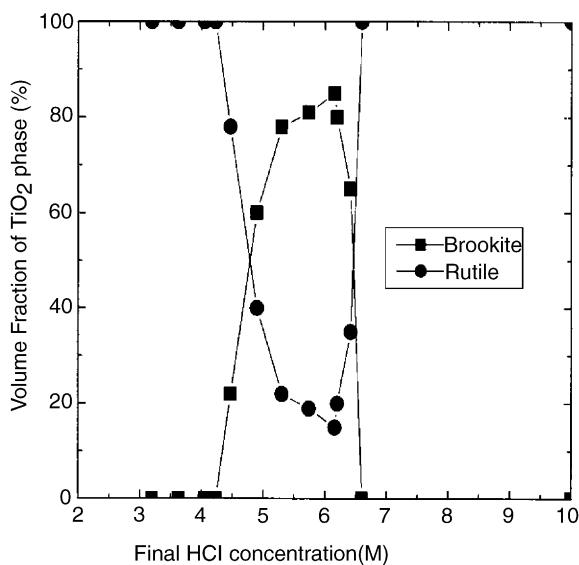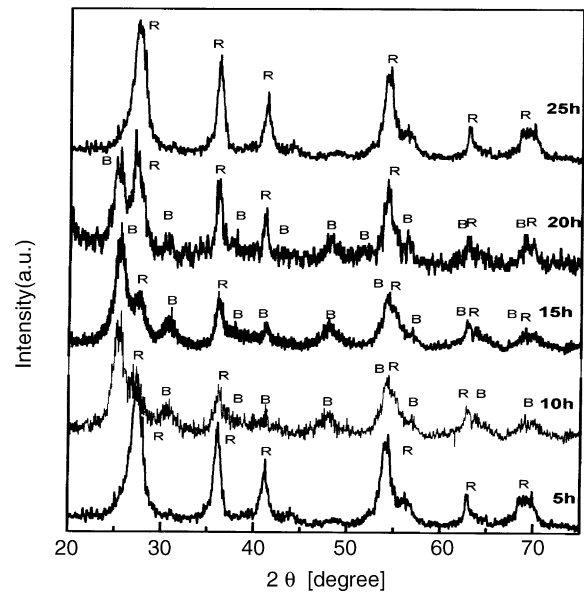

Fig. 3. XRD patterns of TiO_2 particles obtained from aqueous $TiCl_4$ solution with 0.8 M Ti^{4+} prepared by adding 3.0 M HCl at 80 °C according to reaction time.

near 6.6 M even though the concentration difference is very small.

Fig. 3 shows the XRD results of the powders obtained from the aqueous $TiCl_4$ solution with 0.8 M of Ti^{4+} prepared by adding 3.0 M HCl according to various reaction times at 80 °C. The precipitate obtained at 5 h was rutile, a mixture of predominant brookite and rutile at 10–15 h. But, when the reaction time was extended to 20 h the mixture phase, in which the volume fraction of brookite decreased abruptly but increased that of rutile, while a rutile phase TiO_2 was formed at 25 h. Then, the obtained amount of powder at 5 h was about 17.5% of that theoretically available amount of TiO_2 from the aqueous $TiCl_4$ solution. At 10 h, that was increased to about 70% and a mixture phase, whose ratio of brookite to rutile by volume was 75 to 25, was formed. In this case, because the theoretically available amount of rutile becomes about 17.5%, it can be concluded that the amount of rutile formed at the beginning could be regarded as not changed and the precipitate formed after more than 5 h is brookite. Also, at 15 h about 91% of the theoretically available amount of powder was obtained, whose ratio of brookite to rutile by volume was 81 to 19. As same as the above case, because the theoretically available amount of rutile becomes about 17.3% although there was a little difference when compared to 17.5%, considering the possible error in the step of separation it can be concluded that the precipitate formed after more than 5 h is brookite. But, although there was almost no difference in quantities between the amount at 20 h and that at 15 h the volume fraction of brookite at 20 h decreased to 45%, forming rutile at and after 25 h.

From these above results, considering the low productive efficiency at a relatively short reaction time of 5 h, it can be seen that the amount of HCl self-generated during reaction

Fig. 2. The volume fraction change of brookite and rutile phases with the final HCl concentration in aqueous $TiCl_4$ solution after reaction.

was so small that the appropriate condition for brookite formation was not made, resulting that rutile phase was formed. Then, since the amount of HCl in the solution increased with reaction time, which might provide the solution state preferable for brookite formation, it is considered that the volume fraction of brookite is gradually increased with increase of reaction time up to about 15 h. But, although there was almost no difference in the final concentration of HCl after 15 h because the concentration of Ti^{4+} ions remaining in the aqueous $TiCl_4$ solution was negligible the volume fraction of brookite abruptly decreased at 20 h and finally only rutile phase was formed at 25 h. This result means that brookite as a metastable structure transformed to rutile as a stable one even though the final concentration of HCl in the precipitation solution has been kept in the range of appropriate ratio for brookite formation. Consequently, it can be said that reaction time as well as the final concentration of HCl in the precipitation solution are the decisive factors in determining the volume fraction of brookite and rutile structures in TiO_2 precipitate.

Fig. 4 shows the change of the pH value in the aqueous $TiCl_4$ solutions with reaction time when heating induced the precipitation. Although the aqueous $TiCl_4$ solutions have various initial pH values due to various HCl concentrations, the pH values are almost constant or show little decrease at the early stage and then great decrease after some time, finally being kept constant. This abrupt decrease in the pH value with time agreed with the starting of the large precipitation in the solution. Also, with the decrease of pH value, transparent solutions were changed into opaque solutions to thereby form precipitates. After completion of precipitation, the opaque solutions were changed into transparent and the pH values were kept constant, which means completion of precipitation. Then, as shown in the Fig. 4, the required time achieved
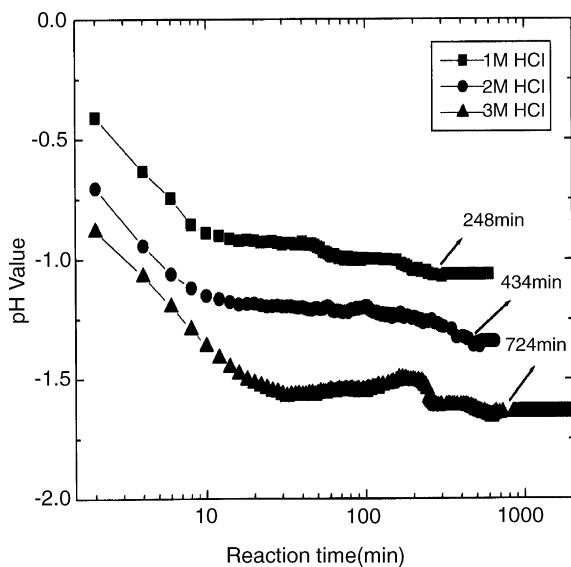
to constant pH value increased with increase in the concentration of HCl added for dilution of the stock solution. That is, the pH value of the solution using 1.0 M of HCl was kept constant after about 248 min, 434 min at 2.0 M HCl, and 724 min at 3.0 M HCl. Then, Kim and coworkers[3,6,7] reported that because precipitation would be hindered by screening effect of others except for H_2O as an oxygen source for producing TiO_2, the precipitation of TiO_2 in the aqueous $TiOCl_2$ solution occurs easily and rapidly when the sufficient amounts of H_2O are supplied. Therefore, it can be said that the reason why the completion time of the precipitation remarkably varies depending on the HCl concentration is that the amount of H_2O decreases with increase of HCl concentration, showing that total precipitation reaction slowly proceeded. Meanwhile, the efficiencies of precipitates in production were calculated from the ratio of the concentration of Ti^{4+} ions remaining in the aqueous $TiCl_4$ solution after precipitation to that of initial Ti^{4+} ions before precipitation. The productive efficiencies so obtained decreased with increase in the concentration of HCl. That is, the productive efficiency of TiO_2 was 99.9% at 1.0 M HCl, 99.0% at 2.0 M HCl, and 94.1% at 3.0 M HCl. From these results, it can be judged that because the amount of H_2O as an oxygen donor necessary for conversion of Ti^{4+} to TiO_2 is decreased with increase of HCl concentration the productive efficiency was decreased, even though the amount of $TiCl_4$ involved in the reaction was constant.

On the other hand, in order to identify the crystallization for the precipitates and the change of structure with heat treatment the TiO_2 powder, a mixture of rutile and brookite phases, obtained at 3.0 M HCl in Fig. 1, was heat treated in atmosphere at 500–1100 °C for 2 h. Fig. 5 shows the XRD patterns of the TiO_2 powders heat treated at various temper-

Fig. 4. The pH value change of aqueous $TiCl_4$ solution with 0.8 M Ti^{4+} prepared by adding 1.0, 2.0, and 3.0 M HCl with reaction time.
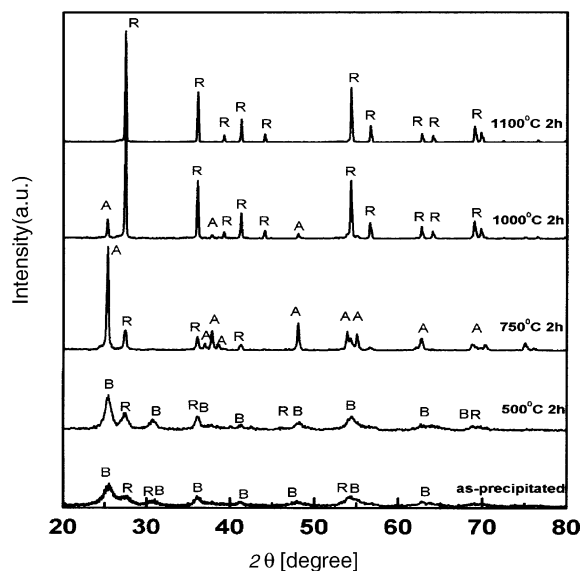

Fig. 5. The XRD patterns of TiO_2 particles with a mixture of brookite and rutile structures after heat treatment at the temperatures of 500–1100 °C for 2 h, respectively (A: anatase; B: brookite; R: rutile).
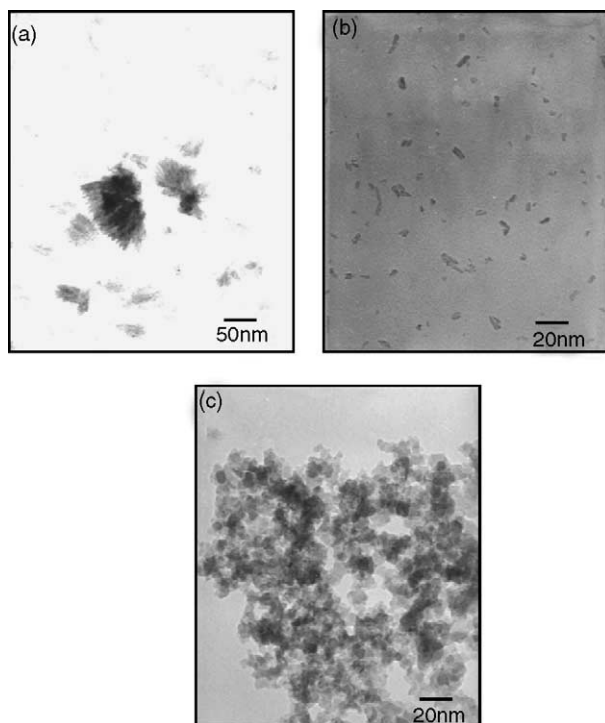
Fig. 6. TEM photographs for rutile-type TiO_2 particles and mixture of brookite and rutile TiO_2 particles prepared from aqueous $TiCl_4$ solution with 0.8 M Ti^{4+} prepared by adding 1.0 M HCl and 3.5 M HCl at 80 °C for 15 h, respectively: (a) agglomerates of rutile particles, (b) well-dispersed rutile particles, and (c) agglomerates of rutile and brookite particles.

atures. When the as-precipitated powder was heat treated at 500 °C for 2 h, all of the peaks for rutile and brookite were grown a little without any change of the crystal structure. This means that the precipitation from the aqueous $TiCl_4$ solution was not by the change of solubility but crystallization, in which crystallite TiO_2 precipitate was already formed. After heat treatment at 750 °C, a changed result, being not accordance with that at 500 °C was obtained, identifying that the peaks characteristic of brookite were disappeared and new peaks corresponding to anatase appeared. Also, as the heat treatment temperature increases the peak intensities for anatase decrease and those for rutile increase and finally, after heat treatment at 1100 °C only the peaks for rutile were observed, indicating that anatase completely transformed to rutile. From these results, it is regarded that brookite was directly not transformed to rutile but rutile via anatase.

Fig. 6 shows transmission electron microscopy (TEM) photographs for TiO_2 particles obtained from the aqueous $TiCl_4$ solutions with 0.8 M of Ti^{4+} prepared by adding 1.0 and 3.5 M HCl. In Fig. 6a is a TEM photograph for rutile particles obtained by using a 1.0 M HCl. Many small particles, although not primary particles, were agglomerated and downy fine particles formed the surfaces of the agglomerates. Fig. 6b is a TEM photograph of the well-dispersed rutile particles (a) using a dispersing agent. Square and spherical particles with a size of about 5–20 nm coexisted. The spe-

cific surface area measured using the BET method was about 130.8 m^2/g. Fig. 6c is a TEM photograph for a mixture phase obtained by using a 3.5 M HCl. This mixture phase was made of about 85% by volume of brookite phase and about 15% by volume of rutile phase. As shown in Fig. 6c, because many particles exist in a state of being agglomerated, unlike pure rutile phase (Fig. 6b), rutile phase and brookite phase were not identified into separate phases. Without phase separation, the specific surface area measured using the BET method was about 194.2 m^2/g.

With respect to the shape of TiO_2 particles, Pottier et al.[2] reported that brookite and rutile phases obtained via thermolysis of aqueous $TiCl_4$ solution have the shape of sphere and elongate spindle, respectively. Zheng et al.[1,11,12] reported that rutile phase is of long spindle shape, anatase phase is of spherical shape, and brookite phase is of cylindrical shape. Kominami et al.[10] reported that anatase phase is spherical or hexahedral and brookite phase is long or cylindrical. Judging collectively from as the above reported results about the shape of crystal structures, rutile phase is generally of elongate shape. However, brookite phase cannot be distinctly identified in appearance. In this point, although it is impossible to distinctly define the particle shape of brookite phase obtained in this study, it is judged that brookite phase is near spherical and rutile phase is linear particles with relatively large aspect ratio.

4. Conclusions

Reaction time and the final concentration of HCl in the precipitation solution are the decisive factors in determining the relative proportion of brookite and rutile structures in TiO_2 precipitate. TiO_2 powder with 50% by volume or more of brookite phase is obtained by heating aqueous $TiCl_4$ solution, whose final concentration of HCl after reaction is kept between 4.9 and 6.4M, at 80 °C for 15 h. Also, the volumetric proportion of brookite is gradually increased with increase of reaction time up to about 15 h but decreased after that time, forming rutile at and after 25 h. The heat treatment results for mixture phase TiO_2 powders, rutile and brookite, showed that brookite phase transformed to anatase, which was finally transformed to chemically stable structure of rutile phase with increase of heat treatment temperature.

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