

Estimation of reaction conditions for synthesis of nanosized brookite-type titanium dioxide from aqueous TiOCl_2 solution

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TiO₂ nanoparticles with a mixture of brookite and rutile phases were prepared from aqueous TiOCl_2 solution at 80–150°C and pure rutile phase at 200°C. The volume fraction of brookite was gradually increased with increase of HCl concentration in the range of about 4.43 M to 6.28 M. The maximum volume fraction of brookite in the as-prepared TiO₂ particles was obtained when oxidation of Ti^{4+} to TiO₂ was completed but it was gradually decreased with increase of reaction time. The reaction time for complete oxidation of Ti^{4+} to TiO₂ was about 15 h at 80°C, about 5 h at 100°C, about 2 h at 120°C, and about 1 h at 150°C, respectively, showing that the kinetics of oxidation is very dependent on the reaction temperature. Brookite phase was not transformed directly to rutile phase but to anatase phase by heat-treatment at about 750°C, which finally converted to rutile phase at 1100°C.

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1. Introduction

TiO₂ has its peculiar physico-chemical properties applicable to various scientific and technical fields [1–3] and exists in three crystal phases; rutile, anatase and brookite [4–6]. Of these the rutile and anatase phases are well known and many studies on their synthesis [1–6], photocatalysis and application for catalyst supports have been reported [4]. On the other hand, only a few studies on the synthesis of brookite-type TiO₂ have been examined [2–11]. It has been reported that pure brookite-type TiO₂ without mixture of rutile or anatase phase is difficult to prepare and the difficulty in preparing brookite having high purity and large surface area is probably one of the reasons for the limited application of brookite-type TiO₂ as a catalyst support and photocatalyst [5, 6]. The uses and performances for a given application are, however, strongly influenced by the crystalline structure, the morphology and the size of the particles [3, 12]. Generally, titanium dioxides are 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 [13–16]. Recently, Zheng *et al.* [6, 7] have studied the preparation condition that leads to brookite formation by hydrothermal method using titanium compounds, such as $\text{Ti}(\text{SO}_4)_2$ and TiCl_4 , as a starting material. Kominami *et al.* [5] synthesized microcrystalline TiO₂ with brookite structure by thermal treatment of oxobis (2, 4-pentanedionato-O,O') titanium in ethylene glycol in the presence of sodium laureate and a small amount

of water. Pottier *et al.* [3] reported that TiO₂ with a mixture of predominant brookite and rutile structure can be formed by thermolysis of TiCl_4 in HCl medium at 100°C and the relative proportions of brookite and rutile are markedly dependent on the acidity of the medium and the concentration of titanium.

In this study, TiCl_4 used as a starting material was hydrolyzed using HCl solution with various concentrations instead of H₂O in attempt to control its acidity so that TiO₂ nanoparticles could be obtained by merely heating it at temperature range from 80°C to 200°C, from that the influence of HCl concentration in the solution, reaction temperature, and reaction time on determination of crystal structure and change of phase content in crystalline TiO₂ particles estimated. Also, structural transformation of TiO₂ particle by heat treatment was examined at the temperature of 500°C to 1,100°C in atmosphere.

2. Experimental procedure

Titanium tetrachloride (99.9%, Aldrich Chemical Co.) was used without any purification as a starting material to prepare TiO₂ particles by precipitation method. TiCl_4 was taken into a reactor installed in circulating bath, whose temperature can be controlled below –5°C by a refrigerator, because the heat of the exothermic reaction explosively generated when TiCl_4 was hydrolyzed. And then 1.0 M HCl solution of an amount of less than stoichiometry, which was calculated based on H₂O content in the HCl solution, was dropwise added to the reactor

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under stirring for inducing hydrolysis of TiCl_4 . During the reaction, yellow cakes of $\text{TiO}(\text{OH})_2$ were formed first, which were then dissolved with added HCl solution to form a TiOCl_2 solution. The concentration of titanium in the as-prepared TiOCl_2 solution was 5.27 M, and this was used as a stock solution for synthesis of TiO_2 . This stock solution remained in a stable state without precipitation, even after six months at room temperature. Finally, HCl solution with concentration of 0.1 M to 8.0 M including the same amount of H_2O was added to TiOCl_2 solution to assist overall hydrolysis reaction $\text{TiCl}_4 + \text{H}_2\text{O} = \text{TiOCl}_2 + 2\text{HCl}$ [14–16], preparing a transparent aqueous TiOCl_2 solution with 0.79 M of Ti^{4+} for precipitation. This stock solution was poured into reactor and placed in the oven for 15 h at the temperature of 80°C to 200°C for precipitation of TiO_2 .

TiO_2 precipitates were filtered using distilled water and membrane filter with a porosity of $0.1\ \mu\text{m}$ to completely remove Cl^- ions from the precipitates. In the initial washing step, the precipitates were washed by dilute HCl solution to remove titanium hydroxide, which might have not crystallized into TiO_2 particles, because it could make the final powder be dried and hardened. And the precipitates were repeatedly cleaned by distilled water. When the pH value of the precipitate was lower than 5, the precipitates were repeatedly cleaned using NaOH solution until the pH value becomes neutral. Finally, the precipitates were dried for 48 h at 60°C to obtain the final particles. All of the chemicals used in this study were of analytical reagent grade. 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 $\text{CuK}\alpha$ ($\lambda = 1.54056\ \text{\AA}$). The size and shape of the prepared ultrafine-sized particles were observed using transmission electron microscope (TEM). After drying the TiO_2 particles at 200°C for 20 h or more, the specific surface area was measured using ASAP 2010 (Micromeritics) according to the BET method. The oxidation ratio of Ti^{4+} to TiO_2 after reaction was obtained by analyzing the concentration Ti^{4+} ion remaining in the aqueous TiOCl_2 solution using ICP-OES (Perkin Elmer Optima 3200).

3. Result and discussion

3.1. Influence of HCl concentration

Fig. 1 shows the XRD patterns of the TiO_2 particles obtained from the aqueous TiOCl_2 solutions, which were prepared by adding HCl solutions with various concentrations as well as distilled water to the stock solution for precipitation of TiO_2 , at 80°C for 15 h. As identified in the Fig. 1, the particles were rutile-type TiO_2 when not more than 1.2 M HCl including distilled water or 4.0 M HCl was used for dilution of the stock solution whereas a mixture of rutile and brookite phases was obtained at 1.5–3.5 M HCl. Particularly, in the case of using 8.0 M HCl, transparent aqueous TiOCl_2 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 pre-

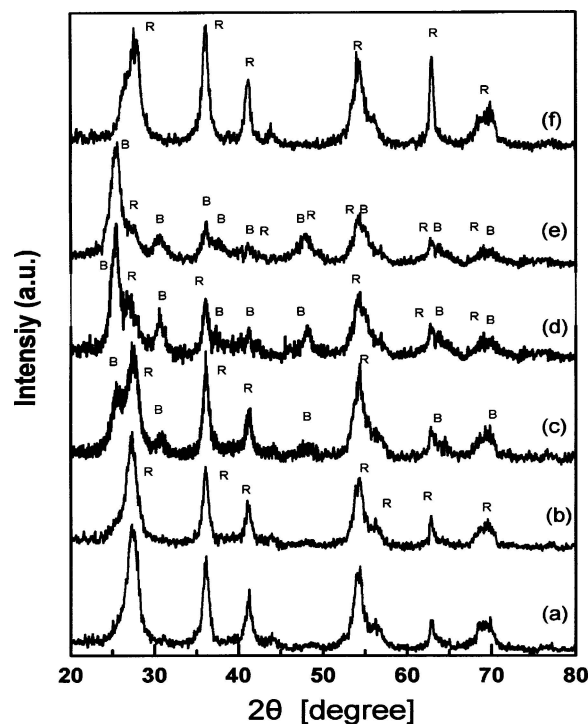


Figure 1 XRD patterns of TiO_2 particles obtained from the aqueous TiOCl_2 solution with 0.79 M Ti^{4+} prepared by adding distilled water (a), 1.2 M (b), 1.5 M (c), 2.0 M (d), 3.5 M (e), and 4.0 M (f) HCl at 80°C for 15 h. (R: rutile, B: brookite).

cipitated. The particles separated by centrifugation of the suspension were rutile phase. Then, with respect to the brookite phase mixed with the rutile phase, because the (120) diffraction peak ($d = 0.3512\ \text{nm}$) of the brookite phase near angle position ($2\theta = 25.3$) overlapped with the (101) diffraction peak ($d = 0.3520\ \text{nm}$) of the anatase phase the peaks of areas except for the angle position were thoroughly examined to identify the formation of brookite phase, showing that all the XRD peaks of the mixture were not assigned to anatase but brookite and rutile phases [5, 8]. From this result, it can be said that the crystal structure mixed with the rutile phase is brookite phase. Also, under the conditions producing the mixture phase, as the concentration of HCl increased the (110) diffraction peak as a main peak of rutile phase decreased, while the (120, 121) diffraction peaks ($d = 0.3512\ \text{nm}$, $0.2900\ \text{nm}$) representing brookite phase increased, meaning that the volume fraction of brookite phase increased. That is, the volume fraction of crystalline structure for TiO_2 particles could be controlled by adjusting the concentration of HCl because the volume fraction of brookite phase varies depending on the HCl concentration. However, it was not possible to obtain the TiO_2 particles with pure brookite structure in this study.

Fig. 2 shows the volume fractions of brookite and rutile phases for the TiO_2 particles obtained from the experiment shown in Fig. 1. Here, the volume fraction of crystal structure for TiO_2 particles was calculated by the K.N.P. Kumar equation using intensities of the (110) main peak of rutile phase and the (120) main peak of brookite phase in the XRD analysis. As shown in the Fig. 2, about 22–26% by volume of brookite phase was obtained at 1.5–1.75 M HCl and 79–85% by volume

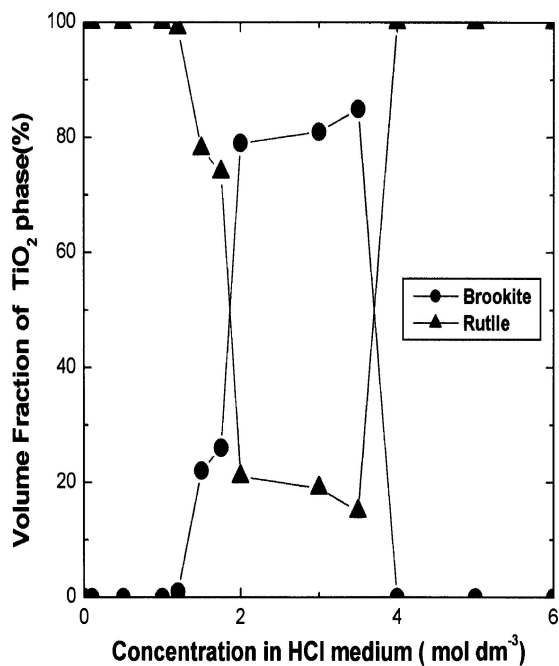


Figure 2 The volume fractions of TiO₂ particles obtained from aqueous TiOCl₂ solution with 0.79 M of Ti⁴⁺ prepared by adding HCl solution with various concentrations.

of brookite phase at 2.0–3.5 M HCl. Particularly, it is interesting that brookite was formed as the main phase (*ca.* 85% by volume) at 3.5 M HCl but disappeared to yield only rutile at 4.0 M HCl although the concentration difference of HCl added to the stock solution for precipitation is small. From this result, it can be judged that there is optimum range of HCl concentration for brookite formation because a mixture phase was obtained at only the condition when 1.5–3.5 M HCl solution was added to the stock solution. Then, because an amount of HCl corresponding to four times of the concentration of Ti⁴⁺ oxidized to TiO₂ is generated as a by-product during reaction, the final concentration of HCl in the solution after reaction becomes an important factor in determining the crystal structure of TiO₂ precipitate and the phase composition of the products. In this regard, based on the conditions producing a mixture phase of brookite and rutile, the range of HCl concentration appropriate for brookite formation was determined from the final concentrations of HCl in the solutions at 1.5 M HCl and at 3.5 M HCl after reaction. Assuming complete oxidation of Ti⁴⁺ ions to TiO₂ because oxidation ratios of Ti⁴⁺ to TiO₂ at the conditions were more than 99.0%, the so-obtained range of HCl concentration is about 4.43 M to 6.28 M although the exact range of HCl cannot be obtained because of insufficient experimental data in subdivided range of HCl concentration.

3.2. Influence of reaction temperature and reaction time

Fig. 3 shows the XRD patterns of the TiO₂ particles obtained from aqueous TiOCl₂ solution, which was prepared by adding 3.0 M HCl to the stock solution, at various reaction temperatures for 15 h. The particles formed at 80–150°C were a mixture of brookite and

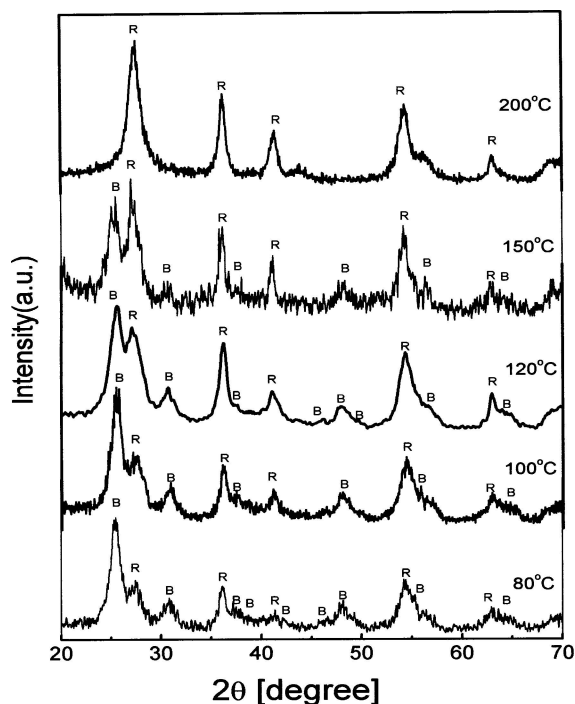


Figure 3 XRD patterns of TiO₂ particles obtained from aqueous TiOCl₂ solution with 0.79 M of Ti⁴⁺ at the temperature of 80°C to 200°C. (R: rutile, B: brookite).

rutile phases and rutile phase was formed at 200°C. As the reaction temperature rises the peaks turn sharper and its intensities are increased, which means that the size of crystallites becomes larger and the crystallinity is increased. Also, under the condition producing the mixture phase, as reaction temperature increases the (120, 121) diffraction peaks (*d* = 0.3512 nm, 0.2900 nm) representing brookite phase decrease but the (110) diffraction peak as a main peak of rutile phase increases, indicating that the volume fraction of brookite phase decreases. In detail, the volume fraction of brookite was about 81% at 80°C, about 71% at 100°C, about 63% at 120°C, and about 45% at 150°C, respectively, showing that the brookite phase content in the crystalline product decreases with increase of reaction temperature and disappears to yield only rutile at 200°C. Particularly, TiO₂ particles obtained at reaction time of 0.5 h was pure rutile without brookite phase regardless of reaction temperature while a mixture phase, in which the volume fraction of brookite was increased to maximum but decreased, was obtained when reaction time was extended. On the other hand, the reaction time necessary for complete oxidation of Ti⁴⁺ to TiO₂ was about 15 h at 80°C, about 5 h at 100°C, about 2 h at 120°C, and about 1 h at 150°C, respectively, indicating that the kinetics of oxidation is very dependent on the reaction temperature while the volume fractions of brookite in the particles obtained at those times were almost same of about 81% regardless of reaction temperature. Then, comparing this result with those obtained at reaction time of 15 h in the above, the volume fraction of brookite markedly decreased when reaction time was extended. This result means that the brookite formed before complete oxidation is gradually transformed to rutile. That is, although the volume fraction of brookite is increased with increase of reaction time

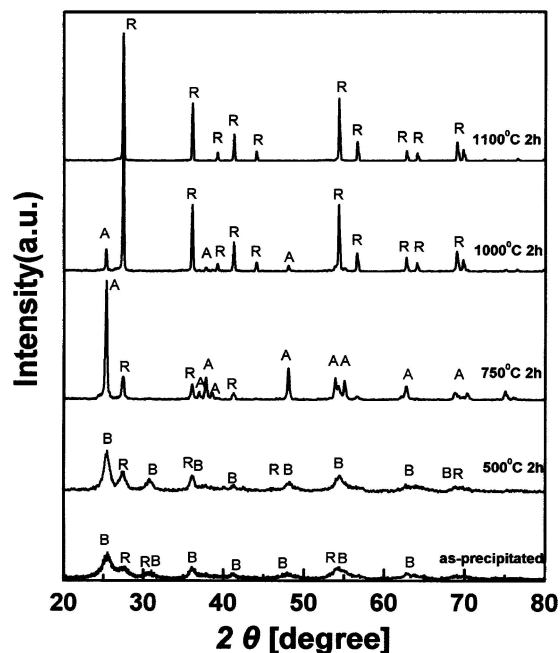


Figure 4 XRD patterns of TiO_2 particles with a mixture of brookite and rutile structures after heat-treatment at the temperatures of 500°C to 1100°C for 2 h, respectively. (A: anatase, B: brookite, R: rutile).

when the HCl concentration is kept in the range for brookite formation because the amount of HCl generated as a byproduct by oxidation might provide the solution state preferable for brookite formation, it is

considered that brookite as a metastable structure gradually transformed to rutile as a stable after complete oxidation, thereby incurring that the volume fraction of brookite gradually decreased with increase of reaction time. From all of the results in the above, it can be concluded 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.

3.3. Heat-treated sample

On the other hand, in order to identify the crystallization for the particles and the change of structure with heat treatment, the TiO_2 particles with a mixture of brookite and rutile structures was heat treated at 500°C to $1,100^\circ\text{C}$ for 2 h in atmosphere. Fig. 4 shows the XRD patterns of the TiO_2 particles heat-treated at various temperatures. When the as-prepared particles were heat-treated at 500°C for 2 h, all of the peaks for rutile and brookite were increased a little without any change of the crystal structure. It is, therefore, regarded that the precipitation from the aqueous TiOCl_2 solution was not by the change of solubility but crystallization, in which crystalline TiO_2 precipitates have been already formed at the stage of precipitation. 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

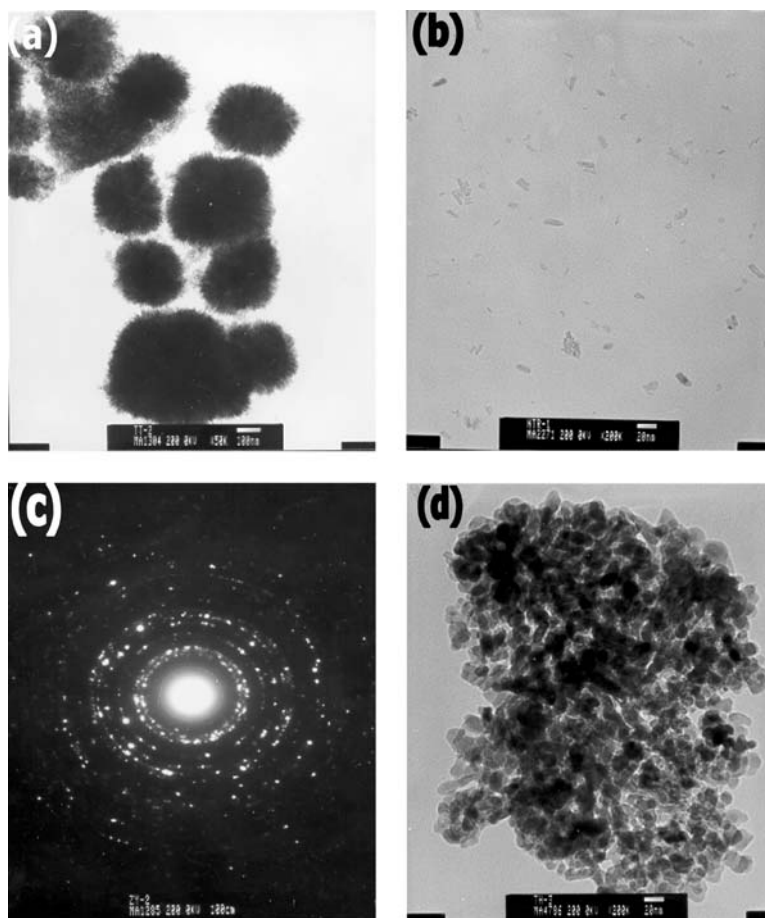


Figure 5 TEM photographs for rutile type TiO_2 particles and the mixture of brookite and rutile TiO_2 particles prepared from aqueous TiOCl_2 solution with 0.79 M Ti^{4+} prepared by adding 1.0 M HCl and 3.0 M HCl at 80°C for 15 h, respectively: agglomerates of rutile particles (a), well-dispersed rutile particles (b), SAD pattern for rutile particle (c), and agglomerates of rutile and brookite particles (d).

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 1,100°C only the peaks for rutile were observed, indicating that anatase completely transformed to rutile through heat-treatment. From these results, it can be said that brookite is directly not transformed to rutile but rutile via anatase.

Fig. 5 shows transmission electron microscopy (TEM) photographs and selected area diffraction (SAD) patterns for TiO₂ particles obtained from the aqueous TiOCl₂ solution with 0.79 M of Ti⁴⁺ prepared by adding 1.0 M and 3.0 M HCl at 80°C for 15 h. Fig. 5a 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. 5b is a TEM photograph of the rutile particles of (a) well-dispersed using a dispersing agent. Almost rectangular particles with a size of about 5 nm to 20 nm coexisted. The specific surface area measured using the BET method was about 133.6 m²/g. Fig. 5c is a SAD pattern for the rutile TiO₂ particles of (b). Because diffraction circles made of points representing crystal directions were distinctly observed, it can be seen that particles are crystalline state. Fig. 5d is a TEM photograph for a mixture phase obtained by using a 3.0 M HCl. This mixture phase was made of about 81% by volume of brookite phase and about 19% by volume of rutile phase and analysis of diffraction line widths in Fig. 1 indicated that the average particle sizes is about 15 nm for brookite and about 12 nm for rutile, respectively. Then, because many particles exist in a state of being agglomerated, unlike pure rutile phase (Fig. 5b), rutile and brookite phases were not identified into separate phases. Without phase separation, the specific surface area measured using the BET method was about 188.5 m²/g. With respect to the shape of TiO₂ particles, Pottier *et al.* [3] reported that brookite and rutile phases have spheroidal and elongated rectangular shapes, respectively. Zheng *et al.* [6, 7] reported that rutile phase is long whiskers with large aspect ratio, anatase phase is short whiskers with a shorter aspect ratio, and brookite phase is double-cone shuttle-like shape. Judging collectively from the above reported results about the shapes of crystal structures, it is considered that rutile phase is generally of elongated rectangular or whisker shape and brookite phase is near spheroidal shape. 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 spheroidal and rutile phase is rectangular shape.

4. Conclusion

Nanosized crystalline TiO₂ particles, consisted of a mixture phase of predominant brookite and small fraction of rutile were synthesized by merely heating aqueous TiOCl₂ solution, in which the concentration of HCl is kept in the range of about 4.43 M to 6.28 M. The HCl concentration in the precipitating solution and reaction time are the decisive factors in determining the volume fraction of brookite and rutile structures in TiO₂ precipitate. The maximum volume fraction of brookite in the as-prepared TiO₂ particles was obtained when oxidation of Ti⁴⁺ to TiO₂ was completed but it was gradually decreased with increase of reaction time because brookite structure directly transformed to rutile. The heat-treatment for TiO₂ with a mixture of brookite and rutile phases, however, 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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