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The crystalline phase stability of titania particles prepared at room temperature by the sol-gel method

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Titania particles having anatase, brookite and rutile phase were prepared at various H^+/TTIP (Titaniumtetraisopropoxide) mole ratios and room temperature by the sol-gel method. The crystalline phases according to the variation of the post heat treatment temperature were observed. The crystalline phase and the phase transformation, morphology, and crystallite size were identified by using XRD, TG/DTA, Raman spectroscopy and TEM. The brookite phase of titania particles prepared at the H^+/TTIP mole ratio of 0.02 and room temperature was not transformed into anatase or rutile even with the heat treatment at 750°C, and also the anatase phase was stable at the temperature as high as 850°C. However, the titania particles prepared at the H^+/TTIP mole ratio of 0.67, which contained the mixed phases of anatase, brookite, and rutile at room temperature, showed only rutile phase at temperature of 750°C. It was thus shown that the initial crystalline phase of the primary particles prepared at room temperature had an important effect on the phase transformation behavior upon post heating. Phase transformation from brookite to anatase and subsequently to rutile occurred with heating.

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1. Introduction

It is well known that titania has three crystalline forms of anatase, brookite and rutile. Among these crystalline forms, rutile phase is the most thermodynamically stable, whereas anatase and brookite are metastable and transformed to rutile on heating. The titania with rutile form has been widely used as pigments, cosmetic ingredients and catalyst support [1, 2]. The anatase form with nanoscale has been recently favored in the field of the photoelectrochemical solar cell (so called, Gratzel type cell) due to its relatively wider band gap property and high surface area [3]. The brookite form has not attracted any attention from investigators because of instability at wide range of temperatures. Also there are little literatures concerning brookite formation and stability. It has therefore been thought that the stability of crystalline phase and phase transformation behavior should be more thoroughtly identified and controlled for better application with increasing use of titania in existing and growing fields such as gas sensor, catalyst support and photocatalyst.

Morales *et al.* [4] investigated the effect of hydrolysis catalyst on crystallite size of titania prepared by the sol-gel method. When no hydrolysis catalyst or HCl catalyst was used, the fresh samples prepared at 70°C were composed of anatase having crystallite size of 13.8 nm

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and a small amount of brookite having crystallite size of 5 nm. After annealing titania powders at 300°C, anatase partially transferred into rutile, but brookite did not change. When the sample was annealed at 600°C, most of anatase and brookite particles transferred into rutile. Bischoff and Anderson [5] investigated the effect of peptization process in the sol-gel preparation of porous anatase titania. They reported that titania particles prepared at room temperature from titanium ethoxide by sol-gel method were of a mixture form with anatase and trace of brookite which was not exactly analyzed by XRD technique because of peak overlapping with anatase. There were no comments on the phase stability and phase transformation behavior with the variation of heat treatment conditions. Kenevey *et al.* [6] studied the stabilization of anatase by dopant introduction to the titania lattice by sol-gel and impregnation techniques. The tungsten concentrations up to 10 wt% raised the phase transformation temperatures from anatase to rutile and brookite to rutile by several hundred degrees while maintaining small particle size. In the case of brookite, the phase transformation to rutile measured by DSC (Differential Scanning Calorimetry) occurred at 340°C.

In this work, we report that the peptizing treatment after hydrolysis and condensation reaction by the sol-gel method can affect the formation of the crystalline phase and the rutile phase as well as brookite can be formed even at room temperature, and that the anatase phase formed initially does not transfer into rutile despite the subsequent heat treatment at the temperature as high as 850°C. Also it is shown that the phase transformation occurs from brookite to anatase and subsequently to rutile with the heating at 900–1050°C.

2. Experimental procedure

Titania sols were prepared at room temperature by dropwise addition of the mixture of titaniumtetraisopropoxide (TTIP) and isopropanol with the mole ratio of TTIP/isopropanol = 1.6 into water with vigorous mixing. The mole ratio of water to TTIP was kept constant at 200 unless otherwise specified. On adding the mixture of TTIP and isopropanol into water, a white hydoxide precipitate was formed. To peptize this precipitate, different amount of concentrated $HNO_3(H^+)$ was added into this precipitate solution. The mole ratio of HNO_3 to TTIP(H^+/TTIP) was varied in the range between 0.02 and 0.67.

Titania sols so obtained were dried in vacuum at room temperature. In order to investigate the phase transformation behavior according to the heat treatment condition, the samples were first hydrothermally treated in an autoclave at 240°C for 12 hr and then heat-treated under the air atmosphere at 500–1050°C for 2 hr. Thus, the data marked with 240°C in the following figures were assigned to the samples which experienced only the hydrothermal treatment at 240°C without further heat treatment at higher temperatures.

The crystalline phase and the phase transformation of titania particles were determined using X-ray diffraction mesurements (Rigaku, D-MAX, Japan) and Raman spectroscopy (Jovin-Yvon, HR1000, France/Coherent, INNOVA60-70, U.S.A). Thermogravimetric and differential thermal analyses (TG/DTA, Setaram, TGDTA92, U.S.A.) were also carried out to see the phase transformation with temperature. The heating rate was kept at 10°C/min under the air flow of 30 cc/min. The crystallite size of titania was estimated by peak-broadening analysis using the Scherrer equation [7]. The morphology was observed with TEM (Jeol Co., 1200EX, U.K).

3. Results and discussion

Fig. 1 shows the TG/DTA curves of titania prepared at the H^+/TTIP mole ratio of 0.02 and with the hydrothermal treatment at 240°C. The weight loss occurred gradually to about 500 °C was thought to be due to evaporation of physically adsorbed water (the first endothermic peak around 200°C) and OH^- groups on surface (the second endothermic peak around 400°C). A broad exothermic peak with some shoulders between 500 and 750°C and a rather sharp peak around 900°C were observed. These exothermic peaks in the temperature zone without further weight loss were thought to be related to the crystalline phase transformation. Meanwhile, the sample prepared at the H^+/TTIP mole ratio of 0.67 revealed the similar TG/DTA curves in the overall shape (Fig. 2), but all the exothermic peaks ended below 700°C, indicating no further phase transformation at higher temperatures.

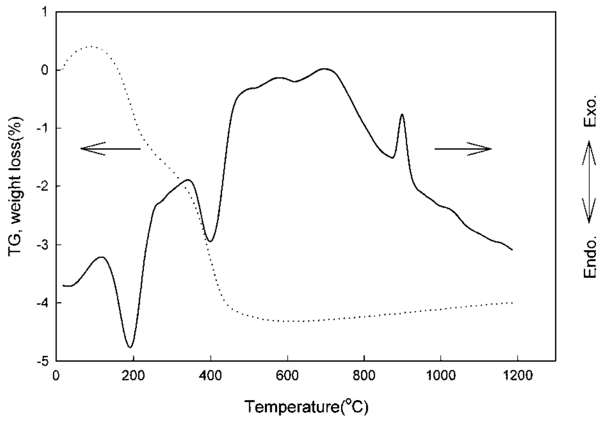


Figure 1 TG/DTA curves of titania particles prepared at the H^+/TTIP mole ratio of 0.02 and with hydrothermal treatment at 240°C for 12 hr.

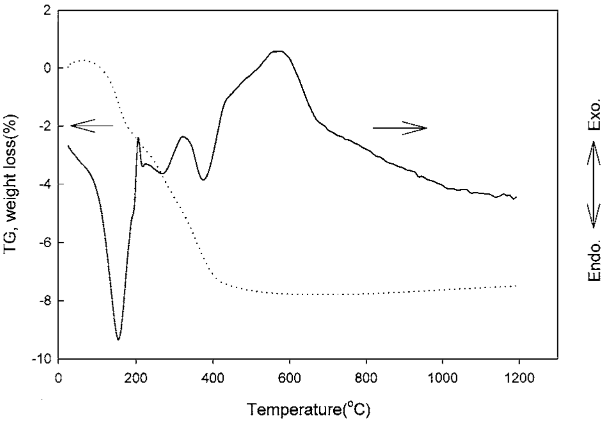


Figure 2 TG/DTA curves of titania particles prepared at the H^+/TTIP mole ratio of 0.67 and with hydrothermal treatment at 240°C for 12 hr.

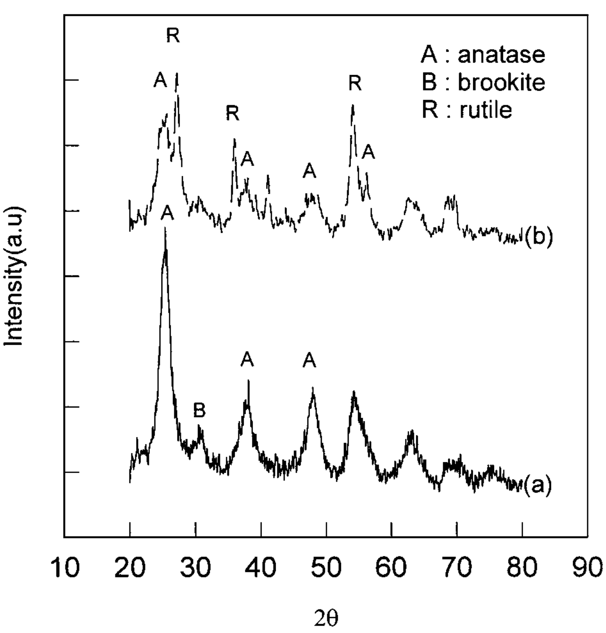


Figure 3 XRD patterns of titania particles prepared at room temperature and various H^+/TTIP mole ratios of (a) 0.02 and (b) 0.67.

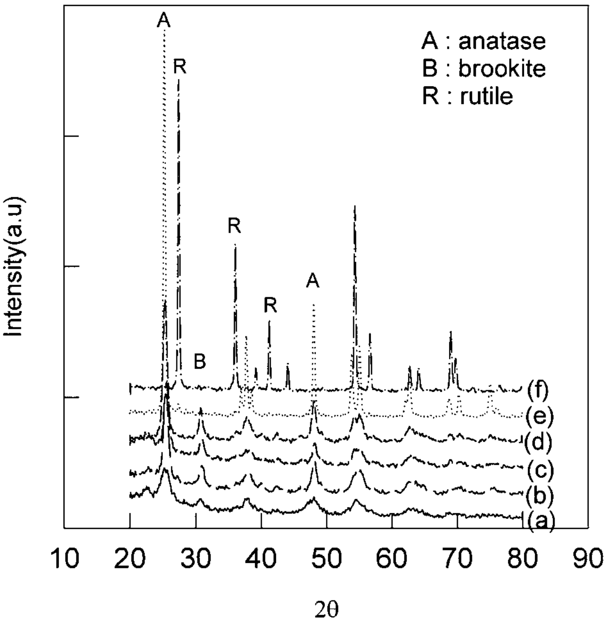


Figure 4 XRD patterns of titania prepared at various heat treatment temperatures of (a) RT, (b) 240, (c) 500, (d) 750, (e) 900, and (f) 1050°C; H^*/TTIP = 0.02.

Fig. 3 shows XRD patterns of titania prepared at room temperature and different H^+/TTIP mole ratios of 0.02 and 0.67. The crystalline phase of titania particles prepared at H^+/TTIP mole ratio of 0.02 indicated a mixture of anatase and brookite. Most of XRD peaks for brookite overlapped with those of anatase particles except the peak obtained at $2\theta = 30.8°$. Crystallite sizes of anatase and brookite prepared at room temperature were estimated to be 3.4–5.8 nm and 2.4–6.0 nm, respectively. The difference of crystallite size between anatase and brookite was not distinct in the initial stage of the synthesis. Titania particles prepared at H^+/TTIP mole ratio of 0.67 were a mixture of anatase and rutile. Brookite phase which was clearly seen in the case of H^+/TTIP mole ratio of 0.02 was scarcely detected. Meanwhile, the samples experienced no peptizing treatment (i.e., H^+/TTIP = 0) indicated the amorphous phase only. It is interesting that such simple control as the variation of H^+/TTIP mole ratio may greatly affect the formation of crystalline phase.

Fig. 4 shows XRD patterns of titania particles prepared at the H^+/TTIP mole ratio of 0.02 according to the variation of the subsequent heat treatment temperature at 500–1050°C under air after the hydrothermal treatment at 240°C. The phase of anatase or brookite was not transformed into rutile even with heating at 750°C. The peak intensity of brookite phase seen at $2\theta = 30.8°$ was rather increased upon heating at 750°C. The phase transformation from brookite to anatase occurred completely at 900°C. And then, the phase transformation from anatase to rutile was completed by further heat treatment at 1050°C. Consequently, this suggests that the phase transformation of brookite might occur through anatase and finally to rutile. The phase transformation behavior like this was not consistent with the results of other literature [6], which suggested a direct transformation from brookite to rutile. Also, the brookite phase formed at room temperature showed the increase in peak intensity with increase of heat treatment temperature (Fig. 4b and d), indicating only the growth of the crystallite size in an appropriate temperature range. The crystallite size of brookite and anatase increased with the heat treatment between room temperature and 750°C from 4.3 to 16.8 nm and from 4.4 to 18.0 nm, respectively. It is again interesting that such a simple peptizing treatment by acid (i.e., HNO_3) could form apparent crystalline phases even at room temperature and that these phases are very stable at a relatively higher heat treatment temperatures compared to other studies.

Fig. 5 shows XRD patterns of titania particles prepared by increasing the H^+/TTIP mole ratio to 0.67. The

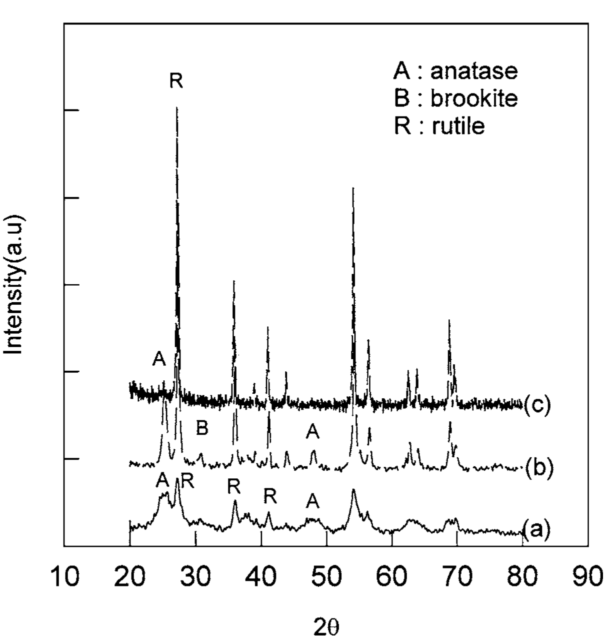
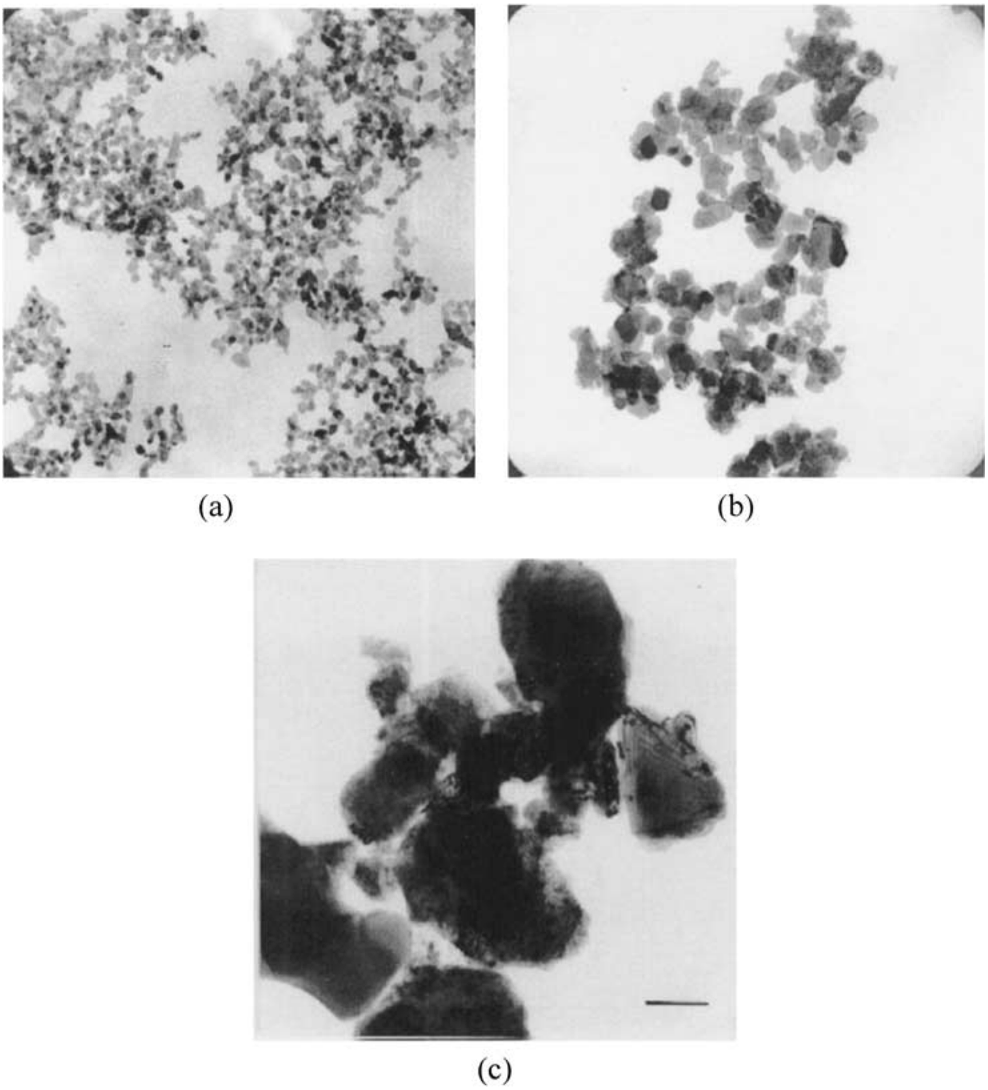


Figure 5 XRD patterns of titania particles prepared at various heat treatment temperatures of (a) RT, (b) 240, and (c) 750°C; H^*/TTIP = 0.67.



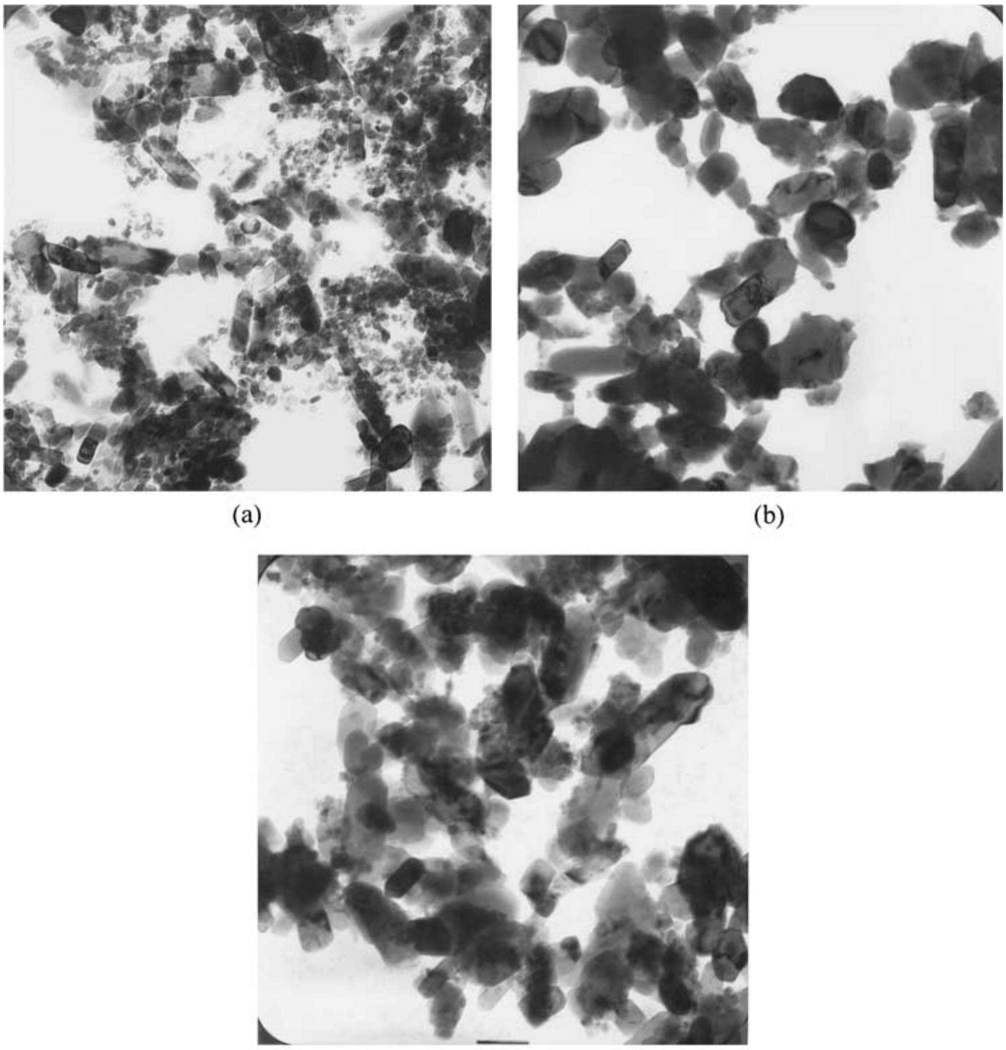
(a) (b) (c)

Figure 6 TEM micrographs of titania particles prepared at various heat treatment temperatures of (a) 240, (b) 900, and (c) 1050°C; $H^+/TTIP = 0.02$ (bar : 100 nm).

titania particles prepared at room temperature were a mixture of anatase and rutile. Brookite phase was not clearly seen from XRD patterns (Fig. 5a). However, when they were hydrothermally treated at 240°C, the XRD pattern indicated an apparent mixture of rutile as a major component and anatase and brookite as minor ones (Fig. 5b). From this result, it was thought that the brookite phase already existed in the sample even though it was hardly seen in Fig. 5a. The titania particles annealed at 750°C showed only rutile phase through phase transformation (Fig. 5c). In contrast to the case of the titania particles prepared at the $H^+/TTIP$ mole ratio of 0.02 (Fig. 4), the phase transformation to a complete rutile phase occurred at a lower heating temperature. The phase transformation route from brookite to rutile was not clear because the intensity of XRD peaks related to brookite and anatase decreased simultaneously with the increase of the heat treatment temperature and the intensity of rutile phase was very strong from the beginning. Thus, it was also not apparent whether the anatase phase was an intermediate in phase transformation from a mixture of brookite and anatase to a complete rutile or not. In this way, the brookite phase was always produced as a minor component under our experimental conditions with those peptizing treatment.

In the case of using titania particles as an inorganic membrane or a catalyst, the problems at high application temperature such as a sintering and phase transformation often result in a decrease of surface area and corresponding loss of activity. It is thus thought that the titania particles having a mixture of anatase and brookite formed at room temperature can be candidate for the retardation of the phase transformation from anatase to rutile and consequently for the prevention of decrease of surface area and activity.

Fig. 6 shows TEM micrographs of titania particles prepared at the $H^+/TTIP$ mole ratio of 0.02 and with the hydrothermal treatment at 240°C and then the heat treatment under air at 900 and 1050°C for 2 hr. As shown in Fig. 6a, the primary particle size of titania particles hydrothermally treated at 240°C was about 10–15 nm. That of titania annealed again at 900°C increased to about 30–40 nm due to crystal growing. The shape of particle was still spherical. However, when the particles were heat-treated at the temperature of 1050°C, the size abruptly increased to about 250 nm. Also, the morphology was changed from sphere to


(a) (b)

(c)

Figure 7 TEM micrographs of titania particles prepared at various heat treatment temperatures of (a) 240, (b) 900, and (c) 1050°C; $H^+/TTIP = 0.67$ (bar : 100 nm).

irregular form. It is notable that the crystal growing is related with phase transformation from anatase to rutile at high temperature.

TEM micrographs of titania prepared at the $H^+/TTIP$ mole ratio of 0.67 are shown in Fig. 7. The crystal growing behavior and the change in morphology with the heat treatment temperature are clearly seen. Compared to the case of Fig. 6, the morphology changed from sphere to rod-like shape at lower temperature. These rod-like particles were stable though the primary particles size increased from about 40–80 nm to 150 nm at temperature as high as 1050°C. The crystal growing rate of titania particles at high temperature was much higher in the case of $H^+/TTIP$ mole ratio of 0.02.

In order to confirm the above difference again, Raman spectra were obtained for both cases of the $H^+/TTIP$ mole ratio of 0.02 and 0.67. As shown in Fig. 8a, several bands appeared at 153, 247, 318, 400, 516 and 639 cm^{-1}. Among these bands, the shoulder band at 153 cm^{-1} and the band with medium intensity at 247 cm^{-1} were assigned to the brookite phase whereas the bands at 400, 516 and 639 cm^{-1} to the anatase phase in agreement with other well known results [8, 9]. Meanwhile, Fig. 8b showed two broad bands at 440 and 612 cm^{-1} ascribed to rutile phase in addition to other bands due to brookite and anatase phases. Cosequently, the existence of three crystalline phases in those titania particles prepared at room temperature could be identified by Raman spectra also.

The XRD results of Fig. 4 according to heat treatment at higher temperatures were re-investigated using Raman spectroscopy as shown in Fig. 9. In the case of titania particles prepared with heat treatment at 500°C (Fig. 9b), most of the Raman bands indicated the anatase phase, especially represented by the band at 144 cm^{-1} which is a strong peak due to anatase phase. It was notable that the bands at 153 and 207 cm^{-1} due to brookite phase of Fig. 9a disappeared completely in Fig. 9c as the heat treatment temperature rose up to 900°C. Only the anatase phase existed at 900°C. As shown in Fig. 9d, after heat reatment at 1050°C, three bands at 236, 440 and 612 cm^{-1} due to rutile phase were obtained.

Fig. 10 shows Raman spectra of titania particles prepared at the $H^+/TTIP$ mole ratio of 0.67, which corresponds to the XRD results of Fig. 5. As shown in

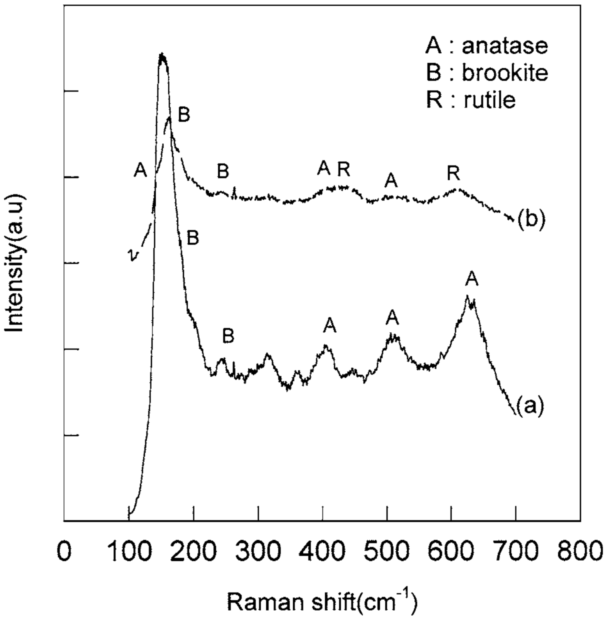


Figure 8 Raman spectra of titania particles prepared at room temperature and various H^+/TTIP mole ratios of (a) 0.02 and (b) 0.67.

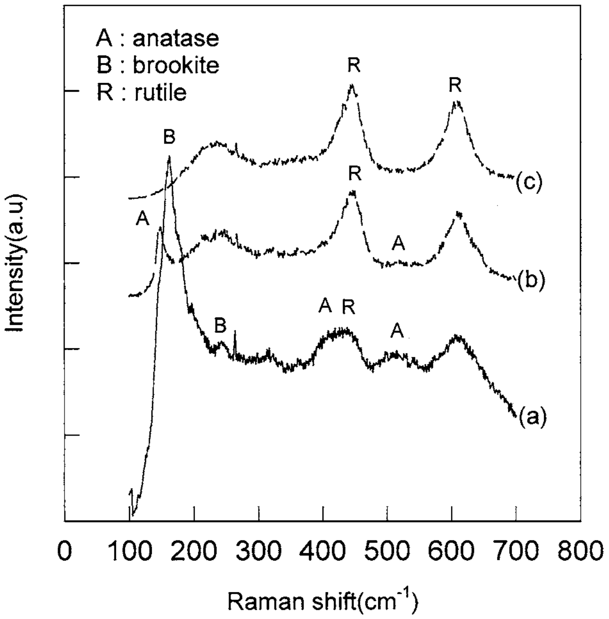


Figure 10 Raman spectra of titania particles prepared at various heat treatment temperatures of (a) RT, (b) 240, and (c) 750°C; H^+/TTIP = 0.67.

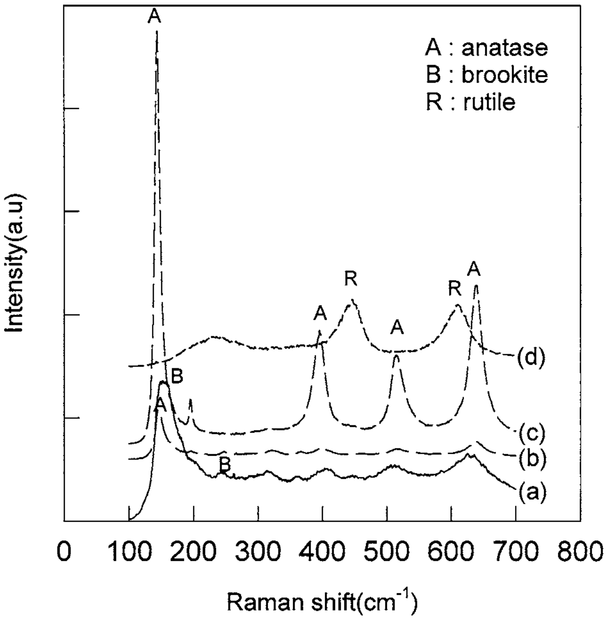


Figure 9 Raman spectra of titania particles prepared at various heat treatment temperatures of (a) RT, (b) 500, (c) 900, and (d) 1050°C; H^+/TTIP = 0.02.

Fig. 10a, several bands due to three crystalline phases were obtained at room temperature. The existence of brookite phase was more clearly detected in Raman spectra than in XRD analysis. The brookite peak at 153 cm^{-1} disappeared after the hydrothermal treatment at 240°C with an appearance of the peak at 144 cm^{-1} as shown in Fig. 10b. At the heat treatment temperature of 750°C, all bands owing to distinct brookite and anatase phases disappeared and only the rutile bands appeared.

Most of the experimental results on phase transformation behavior investigated using Raman spectroscopy revealed the similar trend to those of XRD analysis. Raman spectroscopy was a useful technique to determine the phase composition and phase transformation behavior of titania particles. Especially, brookite phase was clearly seen by using Raman spectroscopy, indicating strong band at 153 cm^{-1}.

4. Conclusion

From the above experimental results, the following were found or suggested; The brookite phase of titania particles prepared at the H^+/TTIP mole ratio of 0.02 and room temperature was not transformed into anatase or rutile even with the heat treatment at 750°C, and also the anatase phase was stable at the temperature as high as 850°C. However, the titania particles prepared at the H^+/TTIP mole ratio of 0.67, which contained the mixed phases of anatase, brookite, and rutile at room temperature, showed only rutile phase at 750°C. Also, the phase transformation from brookite to anatase and then subsequently to rutile occurred with heating. Therefore, the preparation condition such as the H^+/TTIP and H_2O/TTIP mole ratios seems to affect seriously the formation of seed crystalline phase at room temperature and in turn the phase transformation behavior upon the post heating at higher temperatures.

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