Chem. Mater. **1999,** *11,* 2770−2774

Effect of Hydrothermal Treatment of Amorphous Titania on the Phase Change from Anatase to Rutile during Calcination

James Ovenstone and Kazumichi Yanagisawa*

Research Laboratory of Hydrothermal Chemistry, Kochi University, Kochi 780-8520, Japan

Received March 24, 1999. Revised Manuscript Received July 15, 1999

Hydrothermal treatment of amorphous titania has been used to crystallize and stabilize the anatase phase of titania. The hydrothermal treatment conditions can be used to control the physical properties of the crystallized anatase powder, which in turn control the subsequent phase-change properties of the anatase/rutile phase change. The synthesis history of the amorphous starting material is crucial in determining the final phase-change characteristics. The presence of a small amount of brookite phase contamination in the anatase, results in rapid conversion to rutile. Crystallite size also plays an important role in determining the anatase stability, with increasing crystallite size resulting in higher stability, but the phase-change temperature was shown to have only a weak dependence on surface area.

Introduction

Titania has three naturally occurring polymorphs, anatase, brookite, and rutile. Rutile is the thermodynamically stable polymorph at all temperatures and pressures, while anatase and brookite are kinetic products. As a result, all commercially available titania powders contain a mixture of anatase and rutile, and often some brookite too.

The phase change from the anatase polymorph of titania to the rutile polymorph, has been the subject of considerable interest and the focus of many groups' activities over the years.[1−3] Since there is no equilibrium between the polymorphs of titania, there is no specific temperature for the phase changes to occur. The phase change from anatase to rutile has been reported to occur in different temperature ranges from 600 to 1100 °C, depending on the preparation conditions for the anatase. Therefore, many factors which influence the phase change have been investigated, and in particular, the influence of doping ions.[4−7] Although doping ions can play an important role in determining the phase-change characteristics, this is not the whole story, since even in the absence of doping ions, there is a wide range of temperature over which the phase change may occur.[4]

It has been documented in the literature that hydrothermal processing of amorphous titania can result in the production of anatase, which has been shown to have very high photocatalytic activity.[8] Since the anatase phase has a far higher photocatalytic activity than the rutile phase, it is obviously desirable to stabilize the anatase phase as much as possible, but without affecting its photocatalytic activity. Recent results have shown that the control over the hydrothermal conditions, as well as over the contaminant ions present after the amorphous titania production, are vital to control the crystallization properties of the anatase powder.[9,10] In these studies, the importance of the initial synthesis route to the amorphous titania precursor has also been demonstrated.

This paper, however, aims to extend this work and examine the effect of these criteria on the anatase to rutile phase change itself, since varying the original anatase crystallization conditions can greatly influence the phase transition temperature.[11−13] Rao[14] reported that the phase change occurred at around 630 °C, while Shannon[7] quoted a temperature range of 900−950 °C. Kubo[15] reported that the phase transformation could be achieved at room temperature by ball milling. Therefore, changes induced in the anatase powder by changing the crystallization conditions should have a strong effect on the phase transformation.

Experimental Section

The amorphous titania material was made according to the following three methods:

---

(1) Czanderna, A. W.; Rao, C. N. R.; Honig, J. M. *Trans. Faraday Soc.* **1957**, *54*, 1069.

(2) Heald, E. F.; Weiss, C. W. *Am. Mineral.* **1972**, *57*, 10.

(3) Jamieson, J. C.; Olinger, B. *Am. Mineral.* **1969**, *54*, 1477.

(4) Shannon, R. D.; Pask, J. A. *J. Am. Ceram. Soc.* **1965**, *48*, 391.

(5) MacKenzie, K. J. D. *Trans. Br. Ceram. Soc.* **1975**, *74*, 29.

(6) Hishita, S.; Takata, M.; Yanagida, H. *Yogyo Kyokai Shi* **1978**, *86*, 69.

(7) Shannon, R. D.; Pask, J. A. *Am. Mineral.* **1964**, *49* (11−12), 1707.

(8) Kominami, H.; Matsuura, T.; Iwai, K.; Ohtani, B.; Nishimoto, S.; Kera, Y. *Chem. Lett.* **1995**, *11*, 693.

(9) Ovenstone J.; Yanagisawa, K. *J. Phys. Chem. B* **1999**, in press.

(10) Ovenstone J.; Yanagisawa, K. Submitted to Mater. Res. Feb 1999.

(11) Kumar, K.-N. P.; Kumar, P.; Keizer, K.; Burggraaf, A. J.; Okubo, T.; Nagamoto, H.; Morooka, S. *Nature* **1992**, *358*, 48.

(12) Kumar, K.-N. P.; Kumar, J.; Keizer, K. *J. Am. Ceram. Soc.* **1994**, *77* (5), 1396.

(13) Kumar, K.-N. P. *Scr. Metall. Mater.* **1995**, *32* (6), 873. Barringer E. A.; Bowen, H. K. *J. Am. Ceram. Soc.* **1981**, *65*, C199−201.

(14) Rao, C. N. R. *Can. J. Chem.* **1961**, *39*, 498.

(15) Kubo, T.; Kato, M.,; Mitarai, Y.; Takahashi, Y.; Ohkura, K. J. *Chem. Soc. Jpn., Ind. Chem. Soc.* **1963**, *3*, 66.

10.1021/cm990172z CCC: $18.00

(1) $TiCl_4$ (30 mL, 0.273 mol) was diluted with ice cold water (300 mL). A 1.5 M NH_3 solution was added dropwise to the clear $TiCl_4$ solution until the pH was raised from 0.5 to 3.0 (~740 mL). The white precipitate formed was aged for 24 h before washing with water until the pH reached 7. The amorphous powder (A3) was then dried for 24 h at room temperature.

(2) $TiCl_4$ (20 mL, 0.182 mol) was diluted with ice cold water (200 mL), and added dropwise to a 7.5 M ammonia solution. The pH fell from 12.5 to 10.9 as the white precipitate formed. Again the amorphous precipitate was aged for 24 h before washing until the pH reached 9.2. The amorphous powder (B3) was then dried for 24 h at room temperature.

(3) $Ti(OC_2H_5)_4$ (25 g) was added to 550 mL of dry ethanol and mixed thoroughly before being added to a 0.6 M solution of water in ethanol [5.94 mL (0.33 mol) of water in 550 mL of ethanol]. After aging for 25 min, the reaction mixture was centrifuged and washed twice with ethanol before drying in a vacuum desiccator (C3). This method was first outlined by Barringer and Bowen.[16]

The basic crystallization treatment was carried out by dispersing 30 mg of amorphous titania powder in 10 mL of distilled water in an autoclave (20 mL internal volume), and then heating the autoclave to a variety of temperatures and for varying lengths of time. The dried product gives a yield of around 80%.

After treatment in the autoclaves, the powders were washed with water and dried at room temperature under vacuum. The phase was determined by XRD (Rigaku Rotaflex), and the crystallite size was estimated by Scherrer's method. The specific surface area was measured using the three-point BET method using a Yuasa Ionics NOVA 1000 instrument. TG/DTA was carried out on a Seiko SSC5200H system. The TG/DTA apparatus was used to calcine samples by heating at a ramp of 20 °C min^{-1} to 1000 °C (unless otherwise stated), before allowing to cool. The phase of these samples was then checked again by XRD, and the anatase/rutile composition estimated by the method outlined by Spurr and Myers.[17] Raman spectroscopy was carried out using a Kaiser Optical Systems Holoprobe Vpt. System.

Results and Discussion

All three starting materials had similar high specific surface areas, at over 350 $m^2\ g^{-1}$. The A3 powder is considered to have some Cl^- contamination, while the B3 powder is considered to have some NH_4^+ contamination from the initial preparation procedure. The C3 powder is considered to be without inorganic ion contamination. While the B3 and C3 powders are both amorphous, the A3 powder has been shown to be nucleated in the anatase phase by Raman spectroscopy.[9]

Figure 1 shows the amount of rutile formed, after calcination at 1000 °C, of powders hydrothermally treated at different temperatures for varying lengths of time. For the C3 powders, there is general trend to lower quantities of rutile as the reaction time in the autoclave is increased. The trend was strongest for the lowest crystallization temperature (100 °C) and the highest crystallization temperature (350 °C). The temperatures between these extremes showed no particular trend with increasing time.

The above results indicate that there are changes in the mechanism of rutile formation, resulting from the changes in the hydrothermal preparation conditions for the anatase material in terms of reaction time and reaction temperature. Analysis of the phases produced after hydrothermal treatment reveals a very important difference between the powders. Hydrothermal treatment of the C3 powders at low and intermediate temperatures (100−300 °C) results not only in the production of anatase, but also the crystallization of small amounts of a second phase—brookite. At the highest temperature of 350 °C, however, there is no brookite formed.

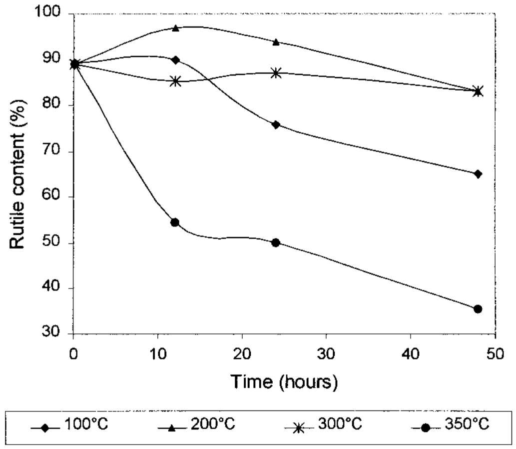

Figure 1. Percent rutile vs time for powders treated hydrothermally at 100 °C, 150 °C, 200 °C, 250 °C, 300 °C, and 350 °C in water and then heated in a DTA apparatus at 20 °C per min to 1000 °C before cooling. Time = 0 refers to powders heated to the specified temperature then cooled rapidly to room temperature. There was no significant reaction during this time period at any temperature.

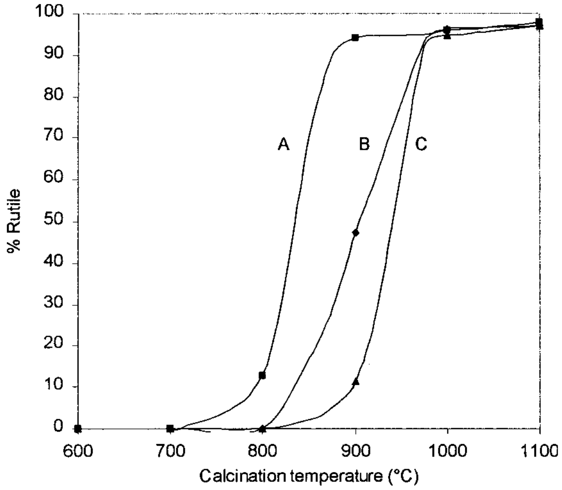

Figure 2. Graph of % rutile formed vs calcination temperature for (A) C3 powder hydrothermally treated for 24 h at 200 °C, (B) C3 amorphous powder, and (C) C3 powder hydrothermally treated for 48 h at 350 °C.

Figure 2 shows how the proportion of rutile increases with calcination temperature for three different C3 powders. It is clear that the transformation occurs faster (at lower temperature) in the hydrothermal product powder containing brookite (A) than the amorphous powder (B), whereas the hydrothermal product powder which did not contain brookite (C) was converted to rutile slower (at higher temperature) than the amorphous powder.

The formation of the kinetically stable brookite under hydrothermal conditions enhances the formation of rutile during the latter calcination stage, since it is not as stable as the anatase polymorph during calcination.

---

[16] Barringer E. A.; Bowen, H. K. *J. Am. Ceram. Soc.* **1981**, *65*, C199−201.

[17] Spurr R. A.; Myers, H. *Anal. Chem.* **1957**, *29* (5), 760.

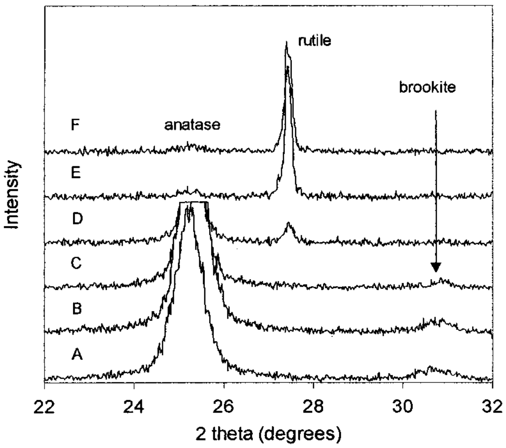

Figure 3. XRD spectra for C3 powder treated hydrothermally at 200 °C for 24 h (A), and then heated in a DTA apparatus at 20 °C per min to (B) 600 °C, (C) 700 °C, (D) 800 °C, (E) 900 °C, and (F) 1000 °C.

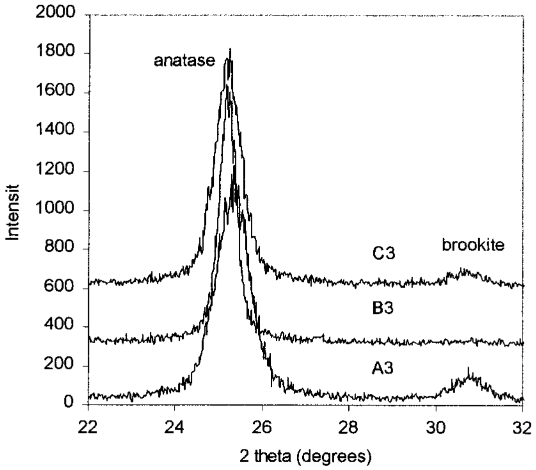

Figure 4. XRD traces for the A3, B3, and C3 powders, hydrothermally treated at 200 °C for 24 h. Note the presence of brookite in the A3 and C3 samples, but not in the B3.

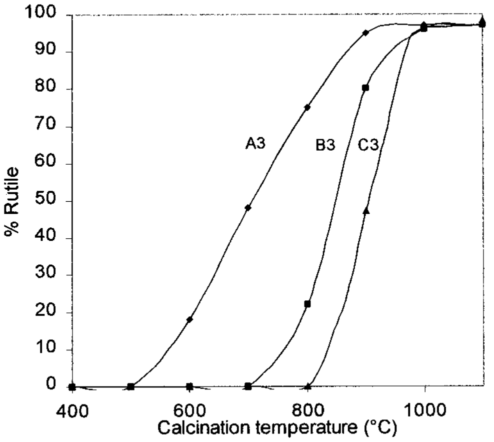

Figure 5. Graph of % rutile formed vs calcination temperature for the precursor powders A3, B3, and C3.

This can be observed by XRD, (Figure 3), where the presence of brookite can be seen in the as produced samples and those calcined at 600 and 700 °C, but disappears as the first rutile crystallites form after calcination at 800 °C. At 800 °C, however, there is no reduction in the amount of anatase formed, which has, in fact, increased in crystallinity. Once the rutile crystallites have formed from the brookite phase, the transition from the anatase to rutile proceeds quickly, as the calcination temperature is further increased. The brookite phase is formed in the low to intermediate temperature range (100−300 °C) to varying extents. These formation temperatures for brookite are in good agreement with those of Oota.[18] At the highest autoclave temperatures, the amount of this phase is reduced, probably by dissolution, and at the longest reaction times removed, thus eliminating its effect on the phase transformation.

The synthesis history of the amorphous titania precursor strongly influences the properties of the powder after hydrothermal treatment; therefore, hydrothermal crystallization of the A3 and B3 powders was carried out over a range of temperatures and times. In addition, since the presence of the brookite phase exerts such a strong influence on the phase change from anatase to rutile, to investigate the effects of other factors such as crystallite size it was necessary to use a different precursor powder. Figure 4 shows the XRD traces for the powders treated at 200 °C for 24 h as a typical example of the different phases formed under hydrothermal conditions. The A3 powder produced a larger amount of brookite than the C3 powder at all reaction conditions, and calcination of the powders led to high rutile proportions in the resulting products. The B3 powder, however, produced only anatase at all reaction conditions. The hydrothermally treated B3 powders, on average, produced less rutile after calcination.

For the B3 powder, unlike the C3 powders, all the hydrothermally treated samples exhibited higher anatase stability than the corresponding amorphous precursor. This can be attributed to the lower activation energy required to form rutile from amorphous powder, since the anatase phase exists at the bottom of an energy well as a kinetically stable product. This applies also to those hydrothermal reactions where there was a considerable amount of uncrystallized amorphous material remaining after treatment, such as in the shortest low-temperature reactions. For the A3 powders, the hydrothermally treated powders were more stable to the phase change than the untreated powders, despite the presence of brookite after hydrothermal processing. However, there may already have been some nucleation of brookite in the untreated A3 powder, as the Raman spectrum shows a high background in the region of the brookite peak at 320 cm^{-1}. The presence of brookite in the starting material seems even more likely since it is clearly present, even in the powders hydrothermally treated at 100 °C for 12 h, unlike the C3 powders, which require higher temperature and longer crystallization times to produce the phase. The presence of brookite nuclei in the starting material would also explain well the extremely rapid conversion to rutile of all the A3 powders (treated and untreated) when compared to the B3 and C3 powders. These results demonstrate the importance of the synthesis history of the amorphous titania precursor in determining the polymorphic conversion characteristics.

Figure 5 shows how the proportion of rutile increases with calcination temperature for three different amor-

---

(18) Oota, T.; Yamai, I.; Saito, H. Yogyo-Kyokai-Shi **1979**, *87* (7), 375.

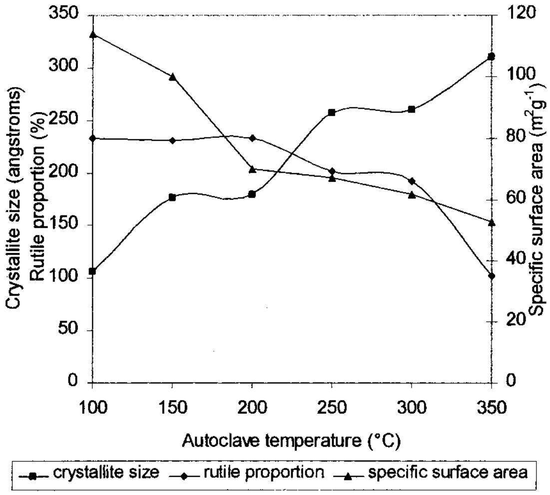

Figure 6. Graphs of crystallite size, specific surface area for B3 powders, hydrothermally treated for 24 h, at various temperatures. Rutile content after calcination at 925 °C is also shown.

phous powders. The figure demonstrates the higher stability of the C3 powder, then the B3, and finally the A3 powder, which is very poorly stabilized in the anatase phase. The difference between the B3 and C3 can be explained by the increase in crystallite size from the B3 to C3 powders, while the very low stabilization of the anatase phase in the A3 powder can be explained both in terms of the low crystallite size, and in terms of the presence of the brookite phase nucleated in the precursor powder. Figure 6 shows graphs of the crystallite size, specific surface area, and the rutile proportion after calcination at 925 °C of B3 powders hydrothermally treated at different temperatures for 24 h. It is clear that an increase in crystallite size results in a reduction of rutile after calcination. The initial increase in size from 100 to 150 °C does not have a corresponding decrease in rutile production because there is still a significant amount of amorphous material left after hydrothermal treatment, and it is this material which produces the high rutile content. It can also be seen that the surface area of the powder has little or no effect on the formation of rutile after calcination. Since poorly crystalline powder, or powder with very small crystallite sizes would contain a larger number of lattice defects, such as interstitial ions, or ion vacancies, it would seem, that the fewer the number of defects present in the crystals, the slower the conversion to rutile. The atoms in these defects have a higher energy than those in the main lattice and can act as nucleation sites for the formation of rutile at the surface of the crystallites.

Acid and base effects in the hydrothermal reaction were also studied. The effects of strongly acidic hydrothermal conditions have been shown to produce phase-pure rutile at high temperatures (>600 °C).[19] Under the present milder regime, however, the use of acidic conditions in the autoclave (0.5 M HCl at 250 °C for 5 h) resulted in the production of mixtures of anatase, rutile, and brookite in the case of the B3 and C3 powders, and anatase and brookite in the case of the A3 powder.

The lack of rutile in the A3 product can be put down to the fact that the anatase was already nucleated before hydrothermal treatment, and so there was no amorphous material available for rutile nucleation. In addition, the solubility of the anatase phase is much lower than that of amorphous titania, and so dissolution/precipitation is also limited. Calcination at 1000 °C, of the products from the A3, B3, and C3 powders, resulted in the production of only rutile in all three cases.

On the other hand, treatment in 0.5 M NH_3 solutions at 250 °C for 5 h produced anatase only for the B3 and C3 powders, and anatase and a little brookite for the A3 powder. Therefore it seems that basic hydrothermal conditions hinder brookite formation, which explains the lack of brookite phase formed by the B3 powders, whose nature was mildly basic. Since even the B3 powder produced brookite under the acid conditions and the C3 powder did not produce any brookite under the basic conditions, it seems reasonable to assume the presence of a few brookite nuclei in the A3 starting material, which was originally precipitated under acidic conditions. After calcination at 1000 °C of the powders formed under basic hydrothermal conditions, the A3 powder was almost completely converted to rutile (93%), while the C3 powder remained predominantly anatase (75%). The B3 powder was left as a mixture of around 75% rutile. The use of distilled water in the absence of either acid or base gave a 95−98% rutile product under the same conditions.

The fact that the prenucleated A3 powder's phase transformation to rutile was least affected by the base, again points to the presence of brookite as the main cause of the change. The stabilization of the anatase phase for the B3 powder under basic hydrothermal conditions was considerably less than for the C3 powder, which also indicates that the main difference was in the amount of brookite formed in the autoclave. The slight improvement in the B3 powder stability can be explained as the removal by dissolution of any nuclei of rutile or brookite which may form in very small quantities under normal hydrothermal conditions.

Studies of heating acidified anatase sols (peptization), showed that the anatase/rutile phase transition temperature can be lowered during subsequent calcination.[11,12] The main difference produced by the peptization was that the process resulted in slightly more crystalline particles, which were able to pack better during the drying process. Since it is considered[13] that a critical nuclei size is required for rapid rutile growth and that the critical size is larger than the normal anatase crystallite size for a sol-produced powder, the improved packing together with increased crystallite size may bring the anatase particles closer to the critical rutile nucleus size. Our results, however, point to a third factor which may contribute to the enhanced phase transition, which is the possible formation of brookite nuclei in the peptization stage of the preparation, since acidic conditions favor this reaction. The XRD patterns shown in refs 11 and 12 show the presence of some brookite phase ($2\theta = 30.7°$). The presence of this second phase should be taken into account when describing the mechanism by which the phase transformation occurs.

Conclusions

Overall, it seems that the most important factor affecting the phase change from anatase to rutile is the

---

(19) Matthews, A. *Am. Mineral.* **1976**, *61*, 419.

presence of a secondary phase, brookite, which results in increasing rutile formation by providing another pathway to nucleation. The second most important factor affecting the phase change is the crystallite size of the anatase. Higher crystallite sizes result in fewer defects in the crystal structure when compared to smaller crystals. This means that the number of potential crystallization nucleation points for rutile is fewer in samples with higher crystallite sizes. Again, this implies that the samples treated for longer times at higher temperature in the autoclave produce more stable anatase. The surface area of the powder is, however, unimportant. The preparation route to the amorphous precursor material controls whether the brookite phase can form. The pH of the hydrothermal solution is also important, since this also influences brookite formation. Low to neutral pH results in a product containing brookite and sometimes rutile, which is easily converted to rutile during calcination. High pH produces only anatase with a high stability during calcination.

Acknowledgment. This project was partly funded by the EU/JSPS Joint Fellowship Programme.

CM990172Z