Hydrothermal Synthesis of Brookite

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Hydrothermal synthesis of brookite was performed at 110-200 °C within 24 h using amorphous TiO_2 and sodium salts as the starting material. Brookite was obtained as an almost single phase at 200 °C and TiO_2 / NaOH mole ratio ≅ 1. By the results of XPS and UV-vis measurements, brookite was considered to be formed from sodium titanate by releasing Na^+ and H^+ of the surface accompanied by oxidation of Ti in the structure.

Recently titanium dioxide has been used in several ways, for example, cosmetic powder, colored glass, anti-fog mirror and so on. Among the polymorphs of titanium dioxide, rutile and anatase have been commercialized. However due to the difficulty of synthesizing pure modification without anatase phase, brookite hasn't been commercialized yet.

It has been found that anatase is the most favorable phase obtained from the amorphous TiO_2 by hydrothermal process, due to the lowest entropy of anatase among the TiO_2-polymorphs (Matthews[1]). Keesmann[2] hydrothermally synthesized rutile, anatase, and brookite from amorphous TiO_2 in NaOH solution and noted that each polymorph has favorable range of pH to be precipitated. Phase boundary between brookite and anatase in Na_2O-TiO_2 system was examined hydrothermally by Watanabe[3] at 250-530 °C for 10 days; brookite is formed under 350 °C and Na_2O / (Na_2O + TiO_2) > 5 mol%, however, sodium titanate was also formed in this condition. Mitsuhashi and Watanabe[4] performed to synthesize brookite from an aqueous solution of $TiCl_4$ and $CaCl_2$ at 220-560 °C for 0.5-220 h and their conclusion was that ionic radii of alkali ion are the most important factor to stabilize the brookite-structure. Oota et al.[5] synthesized brookite in Na-Ti-O-F system at 200-300 °C for 1 days and mentioned that Na(TiO)F-complex would be a precursor of brookite. In these previous studies, brookite was usually obtained as a mixture with other titanium oxides. To synthesize pure brookite, three factors; ratio of alkali ion to TiO_2, duration of the hydrothermal treatment and the pH of solution were taken into consideration in this study. Furthermore, we discussed the structural change of TiO_2 occurred during the crystallization.

Amorphous titanium dioxide (Wako, ~50nm, 99.9%) was used as a starting material of the synthesis. 0.16-1.44 g of the amorphous TiO_2 depending on TiO_2 / NaOH mol ratios shown in Figure 1 was dispersed in 30 ml of distilled water followed by adding 0.18 g of NaOH. Then, the slurry was sealed in the Teflon container and hydrothermally treated at 110-200 °C for 24 h. Products were examined by X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS), FT-IR, UV-vis spectroscopy and Scanning electron microscopy (SEM). The amount of formed brookite was evaluated by the method of Mitsuhashi and Watanabe,[4] using peak intensity ratio $R = I_{br}(121) / [I_{br}(120) + I_{an}(101)]$ obtained from XRD patterns. This ratio corresponds to ~0.9 for ideal brookite.

Depending on the temperature and TiO_2 / NaOH mol ratio, hydrothermal treatment of amorphous TiO_2 leads to the formation of sodium titanate, brookite and anatase (Figure 1).

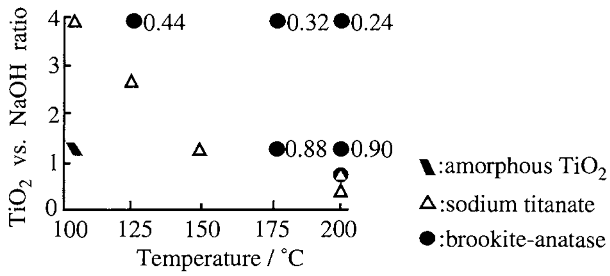

Figure 1. Titamium oxides obtained from amorphous TiO_2 in 0.15 mol/l NaOH solution treated hydrothermally for 24 h.
*The number beside the symbol shows the XRD peak intensity ratio, $I_{br}(121) / [I_{br}(120) + I_{an}(101)]$.

Table 1. Synthetic condition of the titanium oxide using different Na sources (TiO_2 / Na = 4 / 3) hydrothermally treated at 200°C for 24 h and the XRD intensity ratio of brookite to anatase and particle size of the product

Hydrothermal Conditions					
No.	Na source	$pH_{initial}$	pH_{final}	R^a	Particle size by SEM / nm
1	NaOH	12.9	12.7	0.90	300-1000
2	Na_2CO_3	11.3	11.3	0.24	140-180
3	$Na_2B_4O_7$	9.3	9.2	0.16	80-120
4	CH_3COONa	8.0	6.9	0.04	80-120

[a]The XRD peak intensity ratio of $I_{br}(121) / [I_{br}(120) + I_{an}(101)]$.

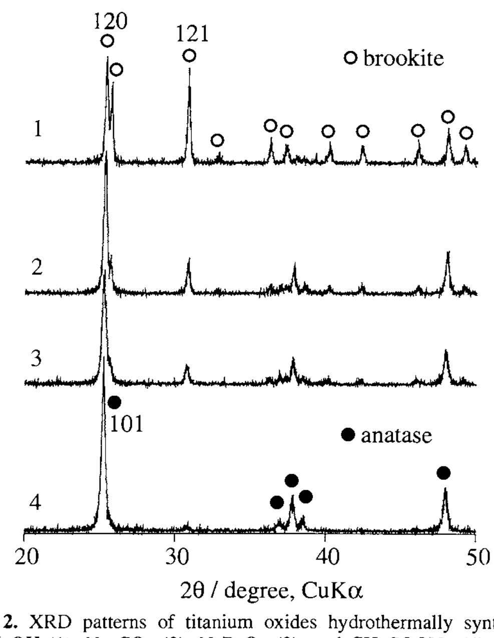

Figure 2. XRD patterns of titanium oxides hydrothermally synthesized using NaOH (1), Na_2CO_3 (2), NaB_4O_7 (3), and CH_3COONa (4) solution (TiO_2 / Na ratio = 4 / 3) at 200 °C for 24 h.

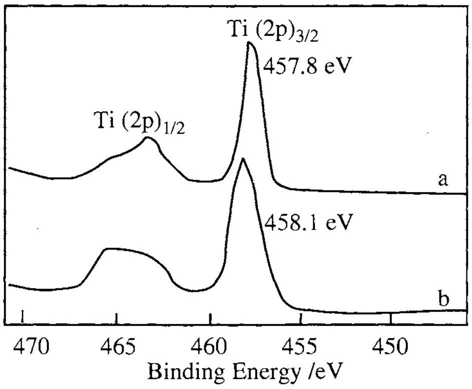

Figure 3. Xp spectra of Ti (2p) of the sodium titanate product (a) and the brookite product (b).

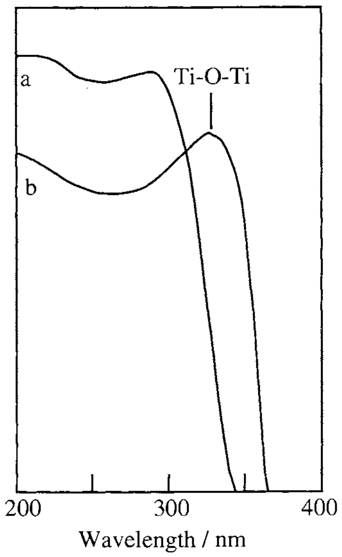

Figure 4. UV-vis spectra of the sodium titanate product (a) and the brookite product (b).

Sodium titanates were formed in conditions along the curve connecting 200 °C, TiO_2 / NaOH = 0.67 and 110 °C, TiO_2 / NaOH = 4. When the temperature and the ratio of the TiO_2 / NaOH became higher, the formation of brookite occurred. At 200 °C, TiO_2 / NaOH ≅ 1, brookite was formed most successfully. With increasing the temperature and the ratio of TiO_2 / NaOH, the amount of anatase increased.

To study the effect of pH, synthesis of brookite was carried out with 0.2 mol/l TiO_2 containing solution of the same TiO_2 / Na ratio (= 4 / 3) using different source of sodium (Table 1). After hydrothermal treatment at 200 °C for 24 h, pH decreased slightly especially in the solution of low pH. The amount of brookite increased with increase in initial pH. When initial pH = 12.9, the R value became 0.9 and the product was considered to be brookite as an almost single phase (Figure 2). As the particle size of the products increased with increase in pH and the size distribution was rather homogeneous in each sample, it is suggested that the crystallization of TiO_2 was slower under higher pH condition.

It has been known that brookite can be formed from Na(TiO)F by releasing Na and F during hydrothermal treatment.[5] It was assumed that brookite would be formed from sodium titanate during the formation of anatase, because brookite was obtained when the crystallization of TiO_2 occurred slowly. To clarify the phase transformation, the starting material (TiO_2 / Na = 4 / 3) was treated hydrothermally in 0.15 mol/l NaOH solution at 200 °C for 2 h and for 24 h. The products were sodium titanate and brookite, respectively. The chemical compositions of the sodium titanate product and the brookite product were analyzed by SEM-EDS. For the sodium titanate product, the atomic ratio was Na-Ti-O = 0.4-1-1.5 roughly corresponding to $Na_2Ti_5O_8$ with much less oxygen than usual sodium titanate having the chemical composition of $Na_2Ti_nO_{2n+1}$. This suggests that Ti is in the state of Ti(III) or Ti(II) in the sodium titanate product. For the brookite product, the atomic ratio was Na-Ti-O = 0.0-1-2.0 corresponding to TiO_2. XPS showed that on the surface of the sodium titanate product Ti was oxidized (Na-Ti-O = 0.5-1-2.6), and Na remained also on the surface of brookite (Na-Ti-O = 0.2-1-2.4). The binding energy value of Ti (2p) spectra was slightly lower in the sodium titanate product (457.8 eV) than that of Ti(IV) in the brookite product (458.1 eV) (Figure 3). FT-IR spectra of the sodium titanate product showed the band at 3500 cm^{-1} and 891 cm^{-1} related to OH-bond,[6] which were absent or diminished in the brookite product. The UV-vis absorption spectrum of the sodium titanate product has an absorption edge in shorter wavelength region than that of the brookite product. Together with the existence of the band at ~220 nm, the sodium titanate is considered to contain tetrahedral coordinated Ti species, and the shift of this band from 250 nm to higher can be attributed to the Ti-O clusters polymerizing to Ti-O-Ti (Figure 4).[7]

From these results, it is suggested that in the alkaline solution, the crystallization of the brookite from the sodium titanate occurred by releasing Na^+ and H^+ accompanied by oxidation of Ti and Ti-OH bond changed to Ti-O-Ti bond in the structure.

Optimum condition of hydrothermal synthesis of brookite was as follows;

TiO_2 / NaOH ~1 using 0.2 mol/l amorphous TiO_2, 200 °C and 24 h hydrothermal treatment.

When temperature of synthesis and TiO_2 concentration of solution become higher than optimum condition, anatase will start to crystallize.

References and Notes

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