Synthesis of brookite-type titanium oxide nano-crystals in organic media

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Thermal treatment of oxobis(2,4-pentanedionato-O,O')titanium (TiO(acac)$_2$) in ethylene glycol (EG) in the presence of sodium laurate and a small amount of water at 300 °C was examined. X-Ray diffraction, transmission electron microscopy and Raman spectroscopy revealed that microcrystalline brookite-type titanium(IV) oxide (TiO$_2$) having an average size of 14×67 nm was formed and that this brookite sample was not contaminated with other TiO$_2$ phases such as anatase and rutile. Sodium salts, water and TiO(acac)$_2$ as the titanium source were indispensable for the formation of brookite crystals and the use of EG as the reaction medium was essential to avoid contamination by other phases. This brookite TiO$_2$ began to directly transform to the rutile phase on calcination at around 700 °C and completely converted at 900 °C.

Introduction

Titanium(IV) oxide (TiO$_2$) is an important industrial material as a main component of paint, pigment, cosmetics and a support for vanadium DeNO$_x$ catalysts. Recently, TiO$_2$ has also received much attention mainly in expectation of being applied to environmental photocatalytic processes such as deodorization, prevention of strains, sterilization[1] and removal of pollutants from air and water.[2–5] TiO$_2$ exists in three crystal phases; anatase, rutile and brookite. The anatase and rutile phases are well known and many studies on their synthesis, photocatalysis and application for catalyst supports have been reported. On the other hand, only a few studies on the synthesis of brookite-type TiO$_2$ have been examined. Kiyama et al.[6] synthesized brookite TiO$_2$ by aerial oxidation of strongly acidic titanium(III) chloride (TiCl$_3$) solution at 95 °C in the presence of sodium acetate. Mitsuhashi and Watanabe[7] found that the brookite form was crystallized by hydrothermal treatment at 220–560 °C of the precipitate prepared from titanium(IV) chloride (TiCl$_4$) and calcium chloride solution. It was reported that the brookite phase was formed on the surface of titanium metal by hydrothermal oxidation in sodium fluoride solution.[8,9] Arnal et al.[10] found that the brookite was formed together with the rutile form by non-hydrolytic sol–gel reaction of TiCl$_4$ and *tert*-butyl alcohol at 110 °C.

It is reported that the brookite phase is partially formed in hydrous TiO$_2$ samples prepared by the precipitation (or sol–gel) method or in samples obtained by calcination of the precipitate (or gel), although the main product is anatase. Music et al.[11] reported that the brookite phase was formed together with anatase in the sample obtained by hydrolysis of titanium(IV) isopropoxide (TIP) in the presence of nitric acid. Brookite was obtained in a sample when the precipitate prepared from TiCl$_4$ and NH$_3$ solutions was aged for 15 months.[12] Zhang et al.[13] found that a small amount of brookite was formed in the sample obtained by hydrolysis of TIP at high temperatures (260–900 °C) in the gas phase. It was reported that a small amount of brookite formed together with anatase phase when the hydrous TiO$_2$ precipitate prepared by the hydrolysis of TIP was calcined at 400 °C.[14] Ye et al.[15] found that a mixture of brookite, anatase and rutile with a ratio of 40 : 33 : 27 was obtained by calcination at 250 °C of hydrous TiO$_2$ prepared by hydrolysis of TiCl$_4$ in the presence of 2-ethylhexanol and sorbitan monooleate in NH$_3$ solution.

These reports suggest that hydrothermal conditions are necessary to obtain brookite-type TiO$_2$ free from contamination by other TiO$_2$ phases. However, large crystals having a small surface area are generally produced by the hydrothermal method and thus-obtained products seems to be not suitable for catalyst supports and photocatalysts because a large surface area is required to increase the active sites and the amount of substrates adsorbed. To our knowledge, there is only one paper in which synthesized brookite TiO$_2$ was successfully used as a catalyst material. Ohtani et al.[16] found that brookite TiO$_2$ prepared by the procedure reported by Kiyama et al.[6] showed high photocatalytic activities for both reactions of dehydrogenation of 2-propanol and silver deposition. The difficulty in preparing brookite having both high purity and large surface area is probably one of the reasons for the limited application of brookite TiO$_2$ as a catalyst support and photocatalyst.

We have examined syntheses of various inorganic compounds in organic solvents as the reaction media at temperatures higher than their boiling points.[17–23] For example, nano-sized anatase-type TiO$_2$ of high crystallinity could be synthesized by hydrolysis of titanium alkoxides in organic solvents with a small amount of water dissolved from the gas phase at temperatures higher than 200 °C and the nanoscale of the products is attributed to the low solubility of TiO$_2$ in the organic media.[17] Higher thermal stability[17,24] and excellent photocatalytic activities[25–28] of this TiO$_2$ have been reported. We also found the formation of nano-sized iron oxides (magnetite and hematite),[19] vanadyl(2+) hydrogen phosphate hemihydrate of high crystallinity[20] and lanthanum diacetate hydroxide (La(OH)(CH$_3$COO)$_2$)[21] in organic media. In this paper, we report a new synthesis method for microcrystalline brookite-type TiO$_2$, without contamination by other TiO$_2$ phases, in organic solvents; we also report the effects of the starting materials and the reaction conditions on the formation of brookite.

Experimental

Synthesis of brookite-type TiO$_2$

The reaction apparatus used for the synthesis of brookite-type TiO$_2$ is shown in Fig. 1. A typical synthesis procedure is as follows: Oxobis(2,4-pentanedionato-O,O')titanium (TiO(acac)$_2$, 0.019 mol) (Tokyo Kasei) and sodium laurate

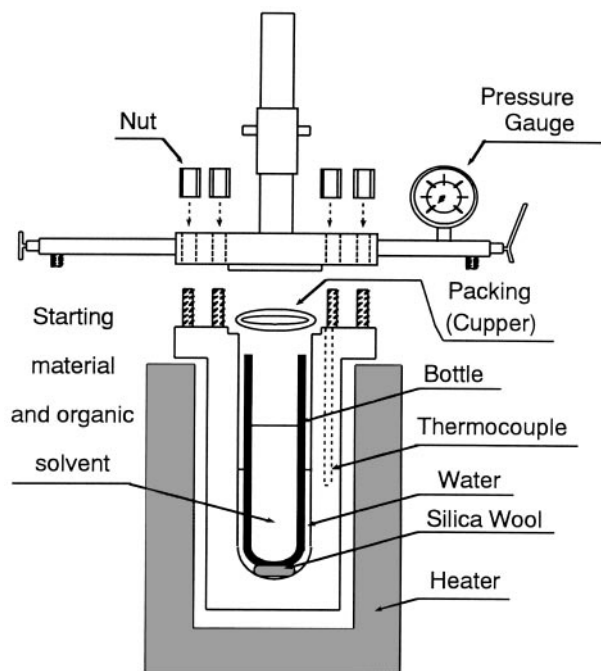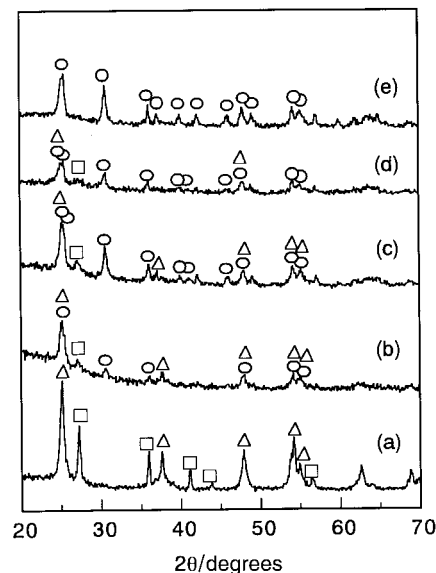**Fig. 1** Reaction apparatus.

Fig. 2 XRD patterns of the products synthesized by the thermal treatment of $TiO(acac)_2$ in the presence of sodium laurate with different sodium–titanium mol ratios in ethylene glycol at 300 °C, Na/Ti = 0 (a), 0.5 (b), 1 (c), 1.5 (d) and 2 (e). Peaks indicated by open circles, open triangles and open squares are assigned to brookite, anatase and rutile, respectively.

(0.038 mol) (Kanto Chemical) were added to 70 cm^3 of ethylene glycol (EG) (Kanto Chemical) in a test tube, which was then set in a 200 cm^3 autoclave. In the gap between the test tube and the autoclave wall, 5 cm^3 of water was added. At this point, the water was not in contact with either $TiO(acac)_2$ or EG. The autoclave was purged with nitrogen, heated at 300 °C at a rate of 2.5 °C min^{-1}, and held at that temperature for 2 h. During the reaction, the water was vaporized and dissolved in the EG. The products were washed first with acetone and then with water repeatedly under sonication, and dried at room temperature. A part of the product was lost in water during the latter washing process because the product consisted of fine particles as discussed later. The product yield in each synthesis was *ca.* 85% on the basis of titanium atom content.

Characterization

Powder X-ray diffraction (XRD) patterns (RINT 2500, Rigaku) were measured using Cu-Kα radiation with a monochromator. The crystallite size of the brookite samples formed was calculated from the half-height width of the 121 diffraction peak of brookite using the Scherrer equation: the value of the shape factor, K, was taken to be 0.9. The morphology and particle size of the product were observed with a transmission electron microscope (TEM) (JEM-3010, JEOL) in the Joint Research Center, Kinki University, operated at 300 kV. Prior to the TEM observation, sample powders were dispersed in distilled water by sonication and then fixed on a copper grid with collodium thin film, which was dried on a filter paper at room temperature. FT-Raman spectra were recorded using a Nicolet Raman 950, with an He–Ne laser (633 nm) using 1 mW laser power, 64 scans and 1 cm^{-1} resolution. IR spectra were recorded *via* the KBr method on a Shimadzu FT-IR 8300 spectrometer. Thermogravimetry (TG) and differential thermal analysis (DTA) were measured on a Rigaku TG-8101 in an air flow of 40 cm^3 min^{-1}. The specific surface areas of samples were calculated using the BET single point method on the basis of nitrogen up-take measured at −196 °C. Calcination of the sample was carried out in a box furnace; the sample in a combustion boat was heated to the desired temperature at a rate of 10 °C min^{-1} and held at that temperature for 1 h.

Results and discussion

Synthesis and characterization of brookite-type TiO_2

Thermal treatments of the mixture of $TiO(acac)_2$ and sodium laurate with various Na/Ti mol ratios in EG were carried out at 300 °C and the XRD patterns of these products are shown in Fig. 2. In the absence of sodium laurate (Na/Ti = 0), the product was a mixture of the anatase and rutile phases and the ratio was estimated to be 75 : 25 by Spurr and Myears' method.[29] Inoue *et al.*[30] examined the thermal treatment of $TiO(acac)_2$ in glycol (glycothermal method) in the absence of water and found that rutile-type TiO_2 was produced together with the anatase-type when EG was used as the solvent, whereas the use of other glycols resulted in the formation of anatase. The present reaction system is different from the glycothermal reaction because a small amount of water was present in this system (see Fig. 1); however, from both sets of results, it is obvious that EG shows a specific solvent effect on the formation of rutile-type TiO_2. Crystallization of the rutile form in the EG medium is now in progress.

When sodium laurate was present in the reaction system (Na/Ti = 0.5), the yield of the rutile form decreased and a new peak characteristic of the brookite structure, *i.e.*, the 121 diffraction peak ($d = 0.2900$ nm), appeared at around $2\theta = 30°$. The fraction of the brookite phase in the product increased when Na/Ti was increased to unity. All the XRD peaks of the product synthesized at Na/Ti = 2 were assigned to brookite (JCPDS No. 29-1360). These results indicated that sodium laurate played an important role in the crystallization of brookite-type TiO_2 in this reaction medium. The 101 diffraction peak ($d = 0.3520$ nm) of the anatase form overlaps the 120 diffraction peak of brookite ($d = 0.3512$ nm). Mitsuhashi and Watanabe[7] estimated the ratio of brookite and anatase in the samples prepared by the hydrothermal method using their XRD intensities, $I_{121}^{brookite}/(I_{120}^{brookite} + I_{101}^{anatase})$. According to their method, the ratio of the brookite and anatase phases in this product (Na/Ti = 2) was calculated to be 1, indicating that this product consists of only the brookite form. The crystallite size of this brookite sample was calculated to be 19 nm from the 121 diffraction peak using the Scherrer equation. Owing to its nano-crystallinity, this brookite sample had a large surface area of 43 m^2 g^{-1}.
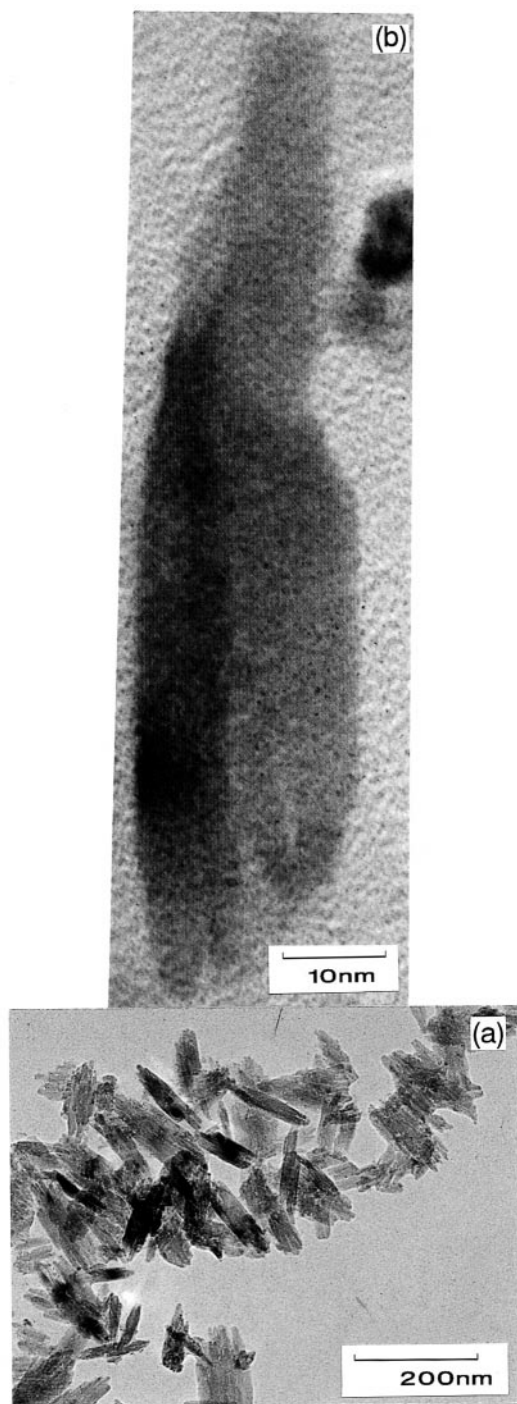
Fig. 3 TEM photographs of the product (Na/Ti = 2): agglomerates (a) and isolated particles (b).

A TEM photograph of the product is shown in Fig. 3(a). The product consists of rod- or columnar-shaped particles and the average size was 14×63 nm. In previous papers, we have reported that nano-sized anatase-type TiO_2 was synthesized by hydrolysis[17,23] or thermal decomposition[22] of titanium alkoxides in organic solvents at high temperatures and that these anatase products were composed of almost spherical or hexagonal particles. Such particles are not observed in Fig. 3(a), which supports the XRD findings that the anatase and rutile forms were not present in this product. A TEM photograph of an isolated particle is shown in Fig. 3(b). Two lattice images were seen throughout this entire particle. Both spacings correspond to the brookite structure, *i.e.*, one is the 121 plane and the other is the 120 or 111 plane. Since the former spacing is characteristic of the brookite structure as

mentioned previously, this result strongly indicates that these particles observed in TEM are brookite TiO_2 crystals.

Raman spectroscopy has been used for the characterization of TiO_2 samples.[11,13,31,32] Tompsett *et al.*[31] measured the Raman spectra of natural and synthetic brookite samples and reported that the brookite phase showed strong peaks at 128, 153, 247, 322 and 636 cm^{-1}. Fig. 4(a) shows the Raman spectrum of the product (Na/Ti = 2); the peaks are in good agreement with those reported by them. Raman peaks of the anatase and rutile forms are observed at 144, 397, 515 and 639 cm^{-1} and 143, 235, 449 and 610 cm^{-1}, respectively.[31] However, peaks due to anatase and rutile were not seen in the spectrum of this product suggesting that the brookite nanocrystals synthesized by the present method are not contaminated with other TiO_2 phases, anatase and rutile.

Fig. 5 shows the FT-IR spectrum of the product (Na/Ti = 2). For comparison, the spectra of the starting materials, $TiO(acac)_2$ and sodium laurate, are also depicted. Peaks assignable to $TiO(acac)_2$ were not observed indicating that
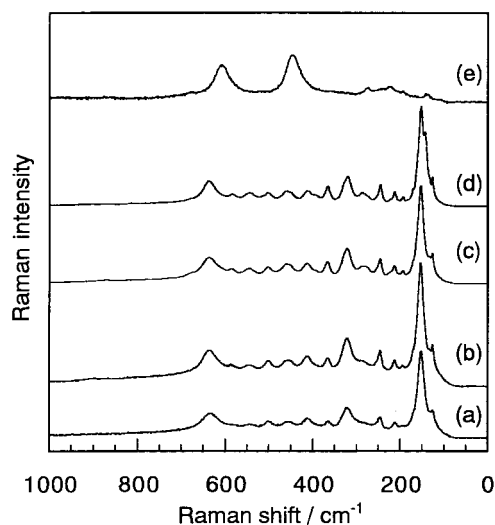

Fig. 4 Raman spectra of the product (Na/Ti = 2) (a) and samples obtained by calcination of the product at 550 °C (b), 700 °C (c), 800 °C (d) and 900 °C (e).
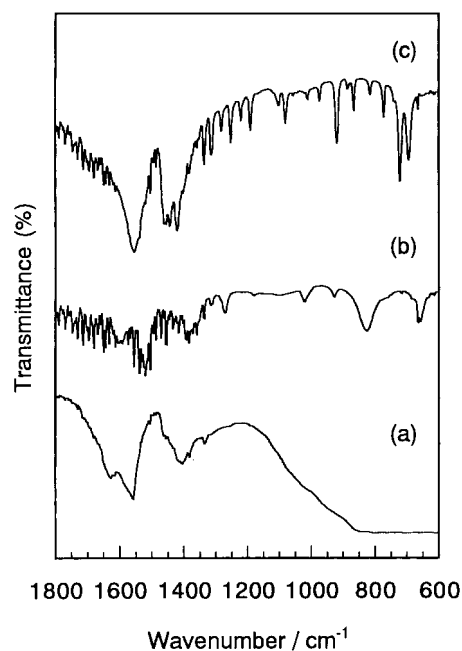

Fig. 5 FT-IR spectra of the product (Na/Ti = 2) (a), $TiO(acac)_2$ (b) and sodium laurate (c).

TiO(acac)$_2$ has completely reacted under these reaction conditions. On the other hand, weak peaks characteristic of EG and laurate groups were observed and these moieties probably adsorbed on the surface of the brookite product. The thermal analysis results are shown in Fig. 6. Weight loss was observed in the range from 200 to 500 °C in the TG curve and the total weight loss up to 1000 °C was 9.44%. An exothermic peak was observed at 289 °C in the DTA curve. Since the absorption peak due to organic moieties disappeared in the IR spectrum of the sample after calcination at 550 °C, the DTA peak is attributed to combustion of these residual compounds. No DTA peak was observed in the high temperature region. X-Ray fluorescence analysis showed that this brookite sample was not contaminated with sodium ions.

Effect of reaction conditions on the formation of brookite

Table 1 summarizes the effects of the presence of alkaline or alkaline earth metals on the formation of brookite TiO$_2$. When sodium acetate was used in place of sodium laurate, the brookite form was produced without contamination by the other phases. The use of other sodium salts of organic acids such as oleic and stearic acids resulted in the formation of brookite although the main phase was anatase. When potassium laurate was used, brookite was formed as the main phase but the product contained the anatase form. Kiyama et al.[6] have synthesized TiO$_2$ by air oxidation of TiCl$_3$ solution, and found that brookite-type TiO$_2$ was produced when sodium acetate was present in the system. They did not refer to the function of sodium or acetate. Their and our results suggest that alkali ions play an important role for nucleation or nucleus growth of the brookite form or prevent nucleation or nucleus growth of the anatase or rutile phase. Ye et al.[15] have
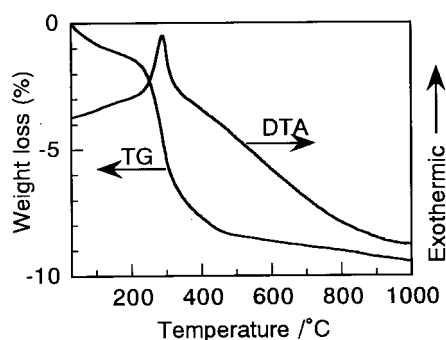

Fig. 6 TG-DTA curves of the product (Na/Ti = 2).

prepared the precursor of brookite by a precipitation process in the presence of surfactant. Sodium laurate is a typical surfactant and its surface-active effect may be also important for the formation of brookite, e.g., dispersion of alkali metals in the reaction medium. Furthermore, these surfactants might directly affect the nucleation of brookite. As shown in Table 1, brookite was formed in the presence of calcium 2-ethylhexanoate.

The effects of the other synthesis conditions are summarized in Table 2. As mentioned in the previous section, a mixture of the anatase and rutile phases was formed in the absence of sodium laurate. The use of titanium alkoxide as the titanium source resulted in the formation of anatase and an unknown phase. The reaction in glycols (1,3-propanediol and 1,4-butanediol) or toluene instead of EG produced the brookite phase as the main product. When the water in the gap between the test tube and the autoclave wall was replaced with the same amount of EG (see Fig. 1), anatase was formed as the sole product. Treatment of TiO(acac)$_2$ in a mixed solvent of EG–water yielded a mixture of rutile and anatase. Although it is difficult to explain these results clearly, the combination of TiO(acac)$_2$, sodium laurate and EG seems to be essential to produce brookite TiO$_2$ without contamination of the anatase and rutile forms. The last two results indicate that water was evaporated and dissolved in the EG during the thermal treatment, and plays an important role in the formation of brookite crystal after being dissolved.

Calcined sample

The brookite product obtained by thermal treatment of the mixture of TiO(acac)$_2$ and sodium laurate (Na/Ti = 2) in EG in the presence of water (5 cm^3) was calcined at various temperatures and XRD patterns after calcination are shown in Fig. 7. A very weak peak due to the rutile phase was observed after calcination at 550 °C, however, the calcined brookite sample showed almost the same crystallite size (20 nm) and surface area (42 m^2 g^{-1}) as the product before calcination. Peaks of brookite became sharper after calcination at 700 °C and the crystallite size increased to 31 nm. The formation of rutile TiO$_2$ was remarkable on calcination at 800 °C and the sample after calcination at 900 °C showed only the rutile phase. Raman peaks due to the brookite phase also became stronger with increasing calcination temperature (Fig. 4(b), (c)). After calcination at 800 °C, a weak peak assignable to the rutile phase was observed in addition to peaks of brookite and the sample after calcination at 900 °C showed only peaks characteristic of the rutile structure. These Raman

Table 1 Effect of alkali or alkaline earth metals on the formation of brookite TiO$_2$[a]

Alkali or alkaline earth metal (M)	M/Ti	Crystal phase[b]	Brookite content[c]
Sodium laurate	0	A, R	0, (25)[d]
Sodium laurate	0.5	A, R, B	0.19
Sodium laurate	1	A, R, B	0.68
Sodium laurate	1.5	A, B	0.73
Sodium laurate	2	B	1
Sodium oleate	1	A, B	0.30
Sodium stearate	1	A, B, unknown	0.32
Sodium acetate	2	B	1
Lithium acetate	2	A	0
Potassium laurate	1.5	A, B	0.49
Potassium laurate	2	A, B	0.66
Potassium acetate	2	A, B	0.35
Magnesium ethoxide	1.5	unknown	—
Calcium 2-ethylhexanoate	2	A, B	0.33
Calcium acetate	1.5	amorphous	—
Strontium acetate	1.5	unknown	—

[a]Oxobis(2,4-pentanedionato-O,O′)titanium was thermally treated together with alkali or alkaline earth sources in ethylene glycol at 300 °C in the presence of 5 cm^3 of water. [b]A: anatase, B: brookite, R: rutile. [c]Calculated from the peak intensity of the brookite and anatase phases according to the equation, $I_{121}^{brookite}/(I_{120}^{brookite} + I_{101}^{anatase})$. [d]Rutile content.

Table 2 Effect of synthesis conditions on the formation of brookite TiO_2[a]

Titanium source[b]	Na/Ti	Solvent A[c]	Solvent B[d]	Phase[e]	Brookite content	Remarks
TiO(acac)$_2$	2.0	EG	H$_2$O	B	1.00	standard conditions
TIP	2.0	EG	H$_2$O	A + unknown	0	effect of titanium source
TiO(acac)$_2$	0	EG	H$_2$O	A, R	0	effect of sodium laurate
TiO(acac)$_2$	2.0	PG	H$_2$O	A, B	0.79	effect of organic solvent
TiO(acac)$_2$	2.0	BG	H$_2$O	A, B	0.51	effect of organic solvent
TiO(acac)$_2$	1.5	toluene	H$_2$O	A, B	0.73	effect of organic solvent
TiO(acac)$_2$	1.5	EG	EG	A	0	effect of H$_2$O
TiO(acac) $_2$	2.0	EG–H$_2$O	EG–H$_2$O	A, R	0	effect of H$_2$O

[a]Titanium source and sodium laurate were thermally treated in solvent A at 300 °C for 2 h. [b]TiO(acac)$_2$: titanium acetylacetonate, TIP: titanium isopropoxide. [c]Solvent (70 cm^3) used as a reaction medium. EG: ethylene glycol, PG: 1,3-propanediol, BG: 1,4-butanediol. [d]Solvent (5 cm^3) added in the gap between the test tube and the autoclave wall. [e]B: brookite, A: anatase, R: rutile.
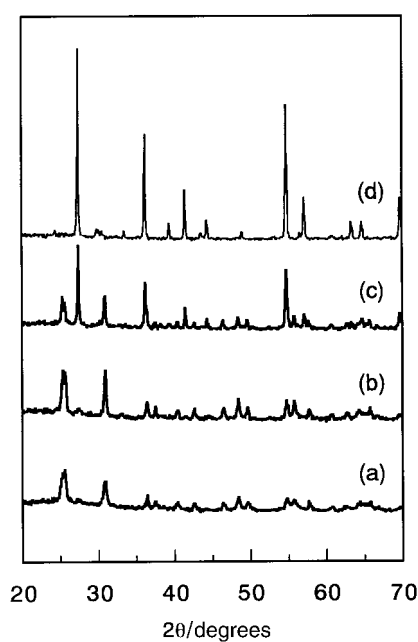

Fig. 7 XRD patterns of the samples obtained by calcination of the product (Na/Ti = 2) at 550 °C (a), 700 °C (b), 800 °C (c) and 900 °C (d).

spectroscopy results are consistent with those of XRD. The anatase form was not observed in either the XRD pattern or the Raman spectrum of any calcined samples, indicating that brookite directly transformed to the rutile phase. As mentioned previously, Ye *et al.*[15] claimed that the brookite phase in the mixture of three phases of TiO$_2$, which had been prepared *via* a precipitation method in the presence of the higher alcohol and the surfactant, transformed to the rutile phase *via* anatase on calcination. The transformation behavior of the brookite phase in their sample is different from that for the present brookite.

TEM photographs of the calcined samples are shown in Fig. 8. The rod-shaped particles were preserved after calcination at 550 °C and their average particle size was 18 × 71 nm. Sintering of particles was observed in the sample calcined at 700 °C and the average particle size increased to 31 × 82 nm. Upon sintering, the surface area decreased to 21 m^2 g^{-1}. Large crystal growth (51 × 101 nm) and different morphology, *i.e.*, rectangular particles, were observed after calcination at 800 °C, which might be due to the formation of the rutile phase.

Conclusions

Microcrystalline brookite-type TiO$_2$ of large surface area was synthesized by thermal treatment of TiO(acac)$_2$ in EG in the presence of sodium laurate and a small amount of water. XRD, TEM and FT-Raman revealed that the thus-obtained brookite product consisted of nano-crystals and was not contaminated
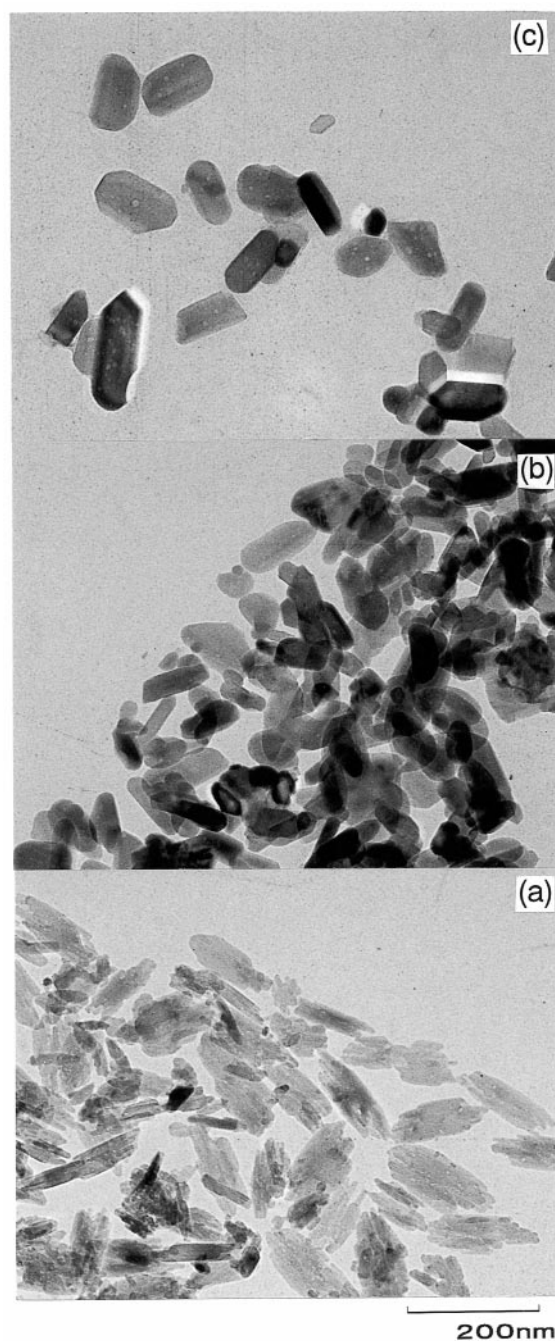
Fig. 8 TEM photographs of the samples (Na/Ti = 2) obtained by calcination of the product (Na/Ti = 2) at 550 °C (a), 700 °C (b) and 800 °C (c).

with the other TiO$_2$ phases (anatase and rutile). EG showed a specific solvent effect for crystallization of brookite TiO$_2$. Both sodium (or potassium) and water are essential for the formation of the brookite phase. The absence of these ions resulted in the formation of a mixture of the anatase and rutile phases, and anatase was formed as the sole product when water was not present in the system. This brookite TiO$_2$ possessed large surface area after calcination at 550 °C and began to transform to the rutile phase directly at around 700 °C.

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