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Phase transformation of protonic layered tetratitanate under solvothermal conditions

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Phase transformation behaviour of the protonic layered tetratitanate, $H_2Ti_4O_9{\cdot}nH_2O$, in air, water, methanol and ethanol has been investigated. $H_2Ti_4O_9{\cdot}nH_2O$ transformed in a series of steps to $H_2Ti_8O_{17}$, monoclinic TiO_2, anatase and rutile. All products retained fibrous morphology similar to that of $K_2Ti_4O_9$ used as the starting material, however, the phase transformation temperature and the microstructure of the products changed significantly depending on the heating environment. Nanosize crystals of TiO_2 possessing high crystallinity could be obtained by solvothermal reactions using water, methanol and ethanol as reaction media.

Introduction

The protonic tetratitanate, $H_2Ti_4O_9{\cdot}nH_2O$, which is formed by ion exchange reaction of $K_2Ti_4O_9$, is known to be applicable as an inorganic ion exchanger,[1,2] a catalyst,[3–7] and a precursor to form other titanate and titania,[8–13] *etc.* It was reported that by heating in air, $H_2Ti_4O_9{\cdot}nH_2O$ transformed to $H_2Ti_4O_9{\cdot}H_2O$, $H_2Ti_4O_9{\cdot}0.5H_2O$ and $H_2Ti_4O_9$ at 70, 120 and 250 °C, respectively,[11] and then to $H_2Ti_8O_{17}$, $TiO_2(B)$, anatase and rutile with increasing temperature.[1,10,11] Another hydrate compound, $H_2Ti_4O_9{\cdot}0.25H_2O$, was also obtained by vacuum drying.[11] $H_2Ti_8O_{17}$ possesses a channel type structure, in which the crystal structure along (101) has some similarity to the (010) projection of $TiO_2(B)$.[1] $TiO_2(B)$ possesses monoclinic structure which has been characterized by a structure composed of edge- and/or corner-linked pairs of octahedra[8,14] and slowly transforms to anatase without weight loss in the temperature range 500–1000 °C.[1,8,10] It was also reported that $TiO_2(B)$ produced by calcining $H_2Ti_4O_9{\cdot}nH_2O$ showed excellent photocatalytic activity,[15] however, there are virtually no reports on the phase transformation behaviour of $H_2Ti_4O_9{\cdot}nH_2O$ in liquid media, *i.e.*, under solvothermal conditions. In previous papers,[16,17] we reported that well crystallized fine particles of anatase possessing excellent sinterability and photocatalytic activity could be obtained by solvothermal reactions using methanol as a reaction medium. In continuation of our studies on the solvothermal synthesis of functional inorganic materials, a series of tests were performed to investigate the phase transformation behaviour of $H_2Ti_4O_9{\cdot}nH_2O$ under solvothermal conditions.

Experimental

Synthesis of $H_2Ti_4O_9{\cdot}nH_2O$

Potassium tetratitanate prepared by a flux method (Otsuka Chemical Co. Ltd., Tokyo, Japan) was used as the starting material. It consisted of a mixture of $K_2Ti_4O_9$ and $K_2Ti_4O_9{\cdot}3H_2O$ possessing fibrous morphology (22–30 μm length and 0.6 μm diameter). After washing with hot water to remove the flux and sizing to < -355 μm, 10 g of the powder was suspended in 1000 cm^3 of vigorously stirred 1 M HCl at 30 °C for 2 h in order to prepare $H_2Ti_4O_9{\cdot}nH_2O$. The product was separated by filtration and washed with distilled water three times, followed by drying at room temperature in a desiccator and at 60 °C in vacuum overnight for the preparation of $H_2Ti_4O_9{\cdot}1.75H_2O$ and $H_2Ti_4O_9{\cdot}0.25H_2O$, respectively. In order to investigate the phase transformation behaviour by solvothermal reactions, 1.0 g of $H_2Ti_4O_9{\cdot}0.25H_2O$ powder were suspended in 75 cm^3 of water, methanol and ethanol. The slurry solution was placed into a SUS 314 stainless steel autoclave of internal volume 120 cm^3 and heated at a given temperature for 1 h. The product was washed with each solvent three times and dried overnight in vacuum at 60 °C. For comparison, $H_2Ti_4O_9{\cdot}1.75H_2O$ was also heated in an electric furnace under air at a given temperature for 1 h, where the heating rate of the furnace was 10° min^{-1}.

Analysis

The K and Ti contents in the sample were determined by inductively coupled plasma atomic emission spectroscopy (ICP, SEIKO SPS 1200A) and atomic absorption flame emission spectroscopy (Shimadzu, AA-6500S), respectively, after dissolving the sample in a HNO_3–HCl mixed solution by boiling for 24 h in a glass covered flask. The phase constitutions of the products were determined by X-ray diffraction analysis

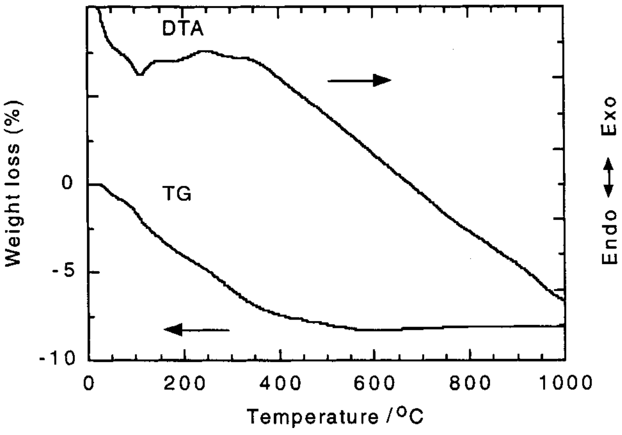

Fig. 1 TG and DTA profiles of $H_2Ti_4O_9{\cdot}0.25H_2O$ prepared by the ion exchange reaction of potassium tetratitanate in 1 M HCl at 30 °C for 2 h followed by vacuum drying overnight at 60 °C.

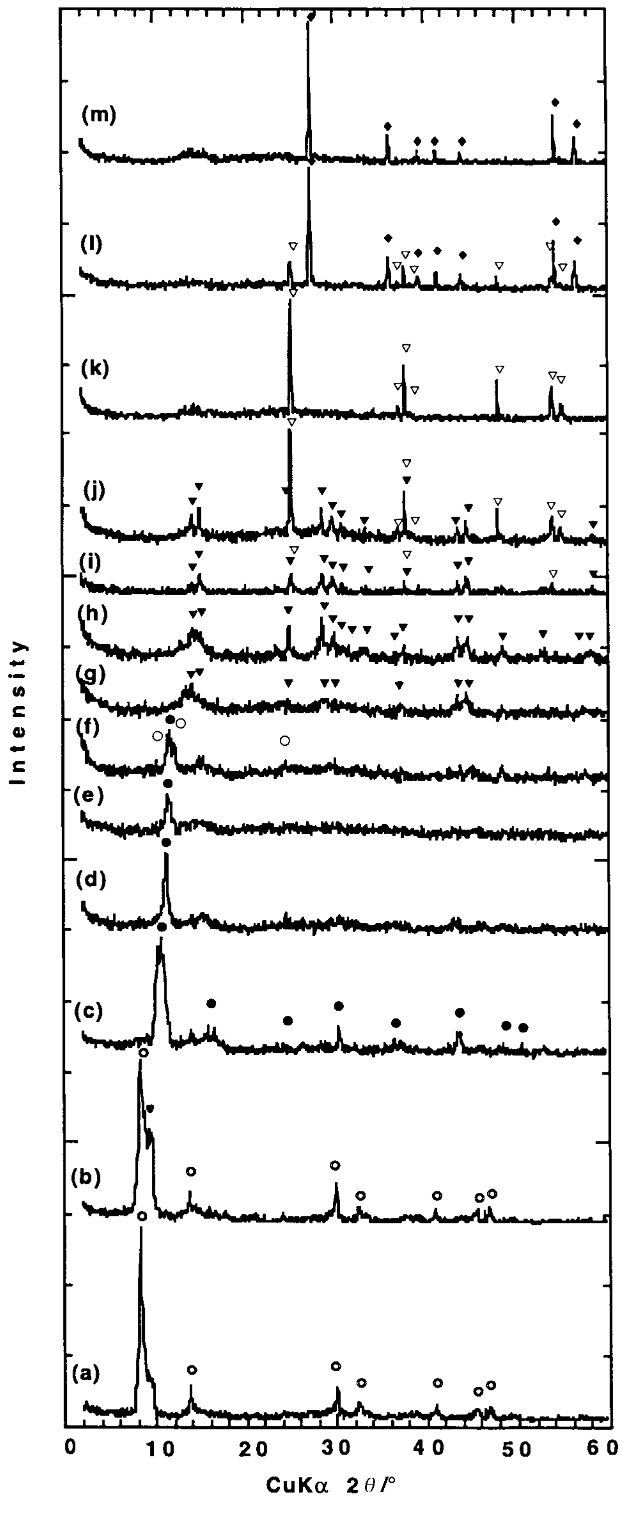

Fig. 2 Phase transformation of $H_2Ti_4O_9{\cdot}1.75H_2O$ by heat treatment in air for 1 h at different temperatures. (a) Before heating; vacuum dried at (b) 25 °C, (c) 80 °C, (d) 105 °C, (e) 150 °C, (f) 200 °C, (g) 300 °C, (h) 550 °C, (i) 650 °C, (j) 850 °C, (k) 1000 °C, (l) 1100 °C, (m) 1200 °C. **○** $H_2Ti_4O_9{\cdot}1.75H_2O$, ♥ $H_2Ti_4O_9{\cdot}H_2O$, ● $H_2Ti_4O_9{\cdot}0.25H_2O$, ○ $H_2Ti_8O_{17}$, ▼ monoclinic TiO_2, ▽ anatase, ◆ rutile.

(XRD, Shimadzu XD-D1) using graphite-monochromatised Cu-Kα radiation and the amount of water in the sample was determined by thermogravimetry and differential thermal analysis (TG, DTA, Rigaku TAS-200). The microstructures of the products were observed by scanning electron microscopy (SEM, Hitachi S-900) and transmission electron microscopy (TEM, JEOL JEM-2010).

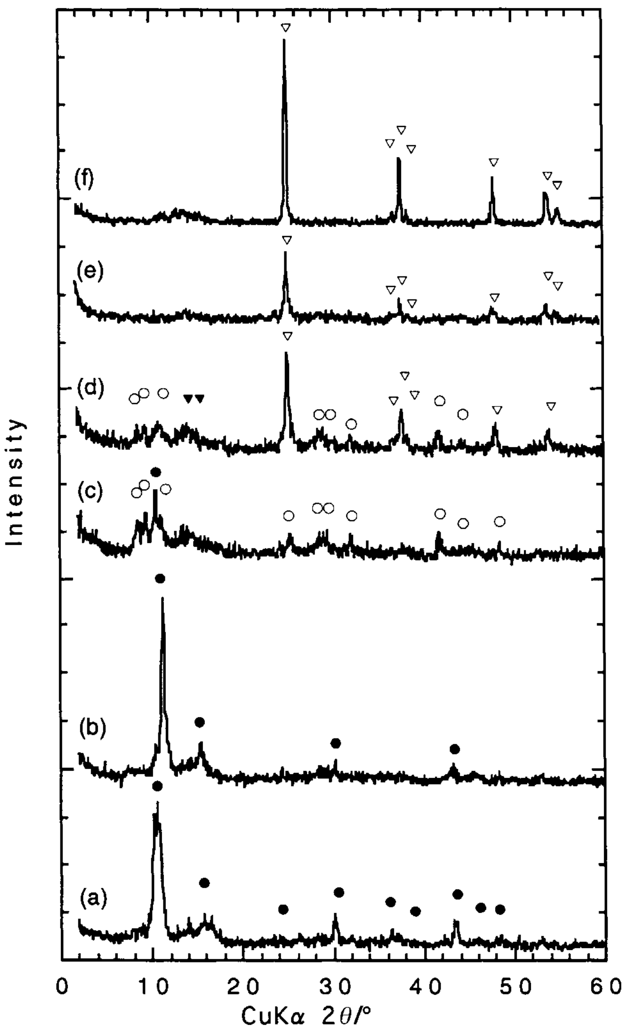

Fig. 3 Phase transformation of $H_2Ti_4O_9{\cdot}0.25H_2O$ (a) by hydrothermal reactions for 1 h at 150 (b), 200 (c), 225 (d), 250 (e) and 325 °C (f). ● $H_2Ti_4O_9{\cdot}0.25H_2O$, ○ $H_2Ti_8O_{17}$, ▼ monoclinic TiO_2, ▽ anatase.

Results

Phase transformation in air

Fig. 1 shows TG and DTA profiles of $H_2Ti_4O_9{\cdot}nH_2O$ prepared by the ion exchange reaction of potassium tetratitanate in 1 M HCl at 30 °C for 2 h followed by vacuum drying at 60 °C overnight. It was confirmed by chemical analysis of the product that >99.9% of K^+ was exchanged with H^+. The sample showed a weight loss accompanied with weak endo- and exothermic peaks over the wide temperature range of 25–600 °C. The weight loss can be attributed to the following dehydration reactions:

$$H_2Ti_4O_9{\cdot}nH_2O \rightarrow H_2Ti_4O_9 + nH_2O \rightarrow$$

$$1/2\ H_2Ti_8O_{17} + (0.5+n)H_2O \rightarrow 4\ TiO_2 + (1+n)H_2O$$

The sample was identified as $H_2Ti_4O_9{\cdot}0.25H_2O$ by powder X-ray diffraction analysis [Fig. 3(a)], yet showed *ca.* 8% weight loss relative to the starting material. Since 6.5% of the weight loss from 100 to 600 °C can be attributed to the dehydration reaction of $H_2Ti_4O_9{\cdot}0.25H_2O$, *ca.* 1.5% of the weight loss up to 100 °C might be attributed to the loss of adsorbed water on $H_2Ti_4O_9{\cdot}0.25H_2O$.

Powder X-ray diffraction patterns of $H_2Ti_4O_9{\cdot}1.75H_2O$ (a) heated at different temperatures are shown in Fig. 2. A mixture of $H_2Ti_4O_9{\cdot}1.75H_2O$ and $H_2Ti_4O_9{\cdot}H_2O$ was obtained after vacuum drying at room temperature (b). With increasing drying temperature, the water in the sample was released

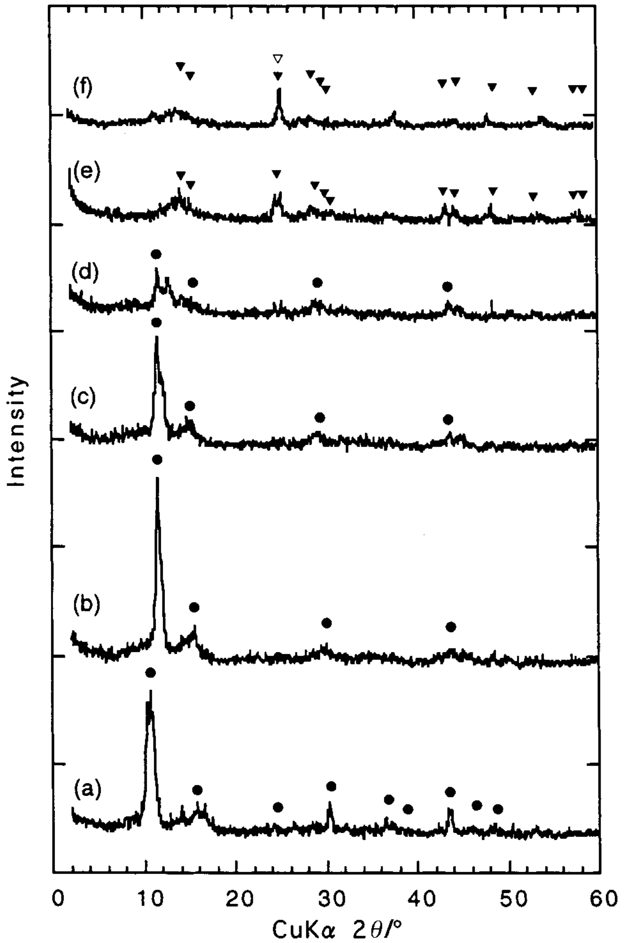

Fig. 4 Phase transformation of $H_2Ti_4O_9{\cdot}0.25H_2O$ (a) by solvothermal reactions in methanol for 1 h at 150 (b), 200 (c), 250 (d), 280 (e) and 325 °C (f). ● $H_2Ti_4O_9{\cdot}0.25H_2O$, ▼ monoclinic TiO_2, ▽ anatase.

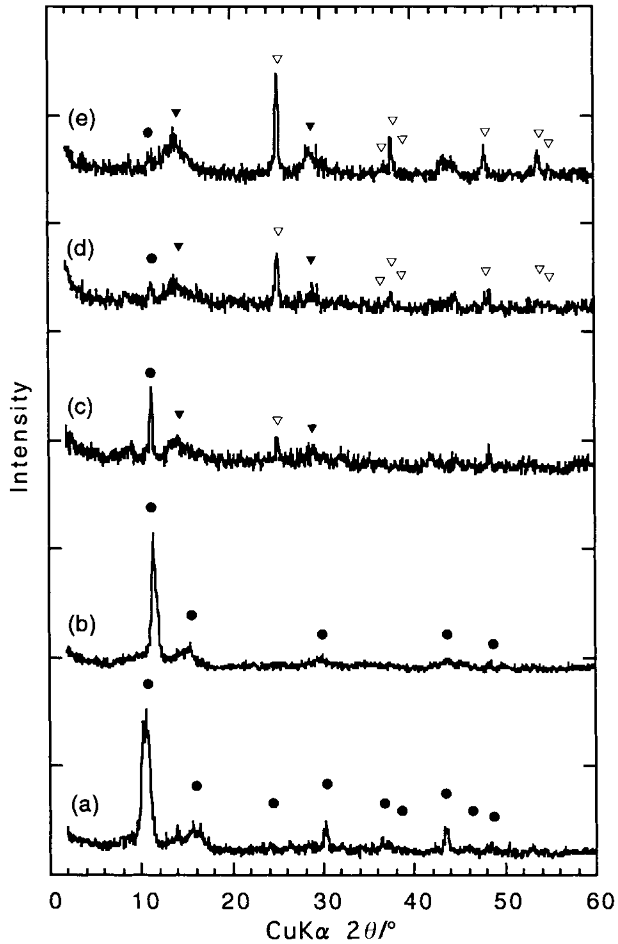

Fig. 5 Phase transformation of $H_2Ti_4O_9{\cdot}0.25H_2O$ (a) by solvothermal reactions in ethanol for 1 h at 150 (b), 200 (c), 280 (d) and 325 °C (e). ● $H_2Ti_4O_9{\cdot}0.25H_2O$, ▼ monoclinic TiO_2, ▽ anatase.

incrementally, and finally, $H_2Ti_4O_9{\cdot}0.25H_2O$ was obtained at 80 °C (c). In the temperature range from 105 to 200 °C, the peak intensity of $H_2Ti_4O_9{\cdot}0.25H_2O$ decreased [(d)–(f)] and peaks corresponding to $H_2Ti_8O_{17}$ appeared at 200 °C (f), indicating that $H_2Ti_4O_9{\cdot}0.25H_2O$ partly transformed to $H_2Ti_8O_{17}$ at 200 °C. Above 300 °C, both $H_2Ti_4O_9{\cdot}0.25H_2O$ and $H_2Ti_8O_{17}$ completely transformed to monoclinic titania [(g), (h)]. The monoclinic titania transformed to anatase at 650–850 °C [(i), (j)], and anatase was obtained as a pure phase at 1000 °C (k). The phase transformation of anatase to rutile began at 1100 °C (l) and was complete at 1200 °C (m). This transformation behaviour of $H_2Ti_4O_9{\cdot}nH_2O$ is similar to that reported by Marchande *et al.*[8,10] although the phase transformation temperatures were a slightly different.

Phase transformation under solvothermal conditions

Fig. 3 shows XRD patterns of the products prepared by hydrothermal treatment of $H_2Ti_4O_9{\cdot}0.25H_2O$ (a) at 150–325 °C. In water, $H_2Ti_4O_9{\cdot}0.25H_2O$ was stable up to 150 °C (b). The phase transformation of $H_2Ti_4O_9{\cdot}0.25H_2O$ to $H_2Ti_8O_{17}$ began at 200 °C (c) which is almost the same as in air, however, the diffraction peaks corresponding to both monoclinic and anatase TiO_2 appeared at 225 °C (d) and anatase was formed as a single phase at a temperature as low as 250 °C (e), 750 °C lower than the phase transformation temperature in air. This indicates that the phase transformation of monoclinic TiO_2 to anatase was greatly promoted under hydrothermal conditions. The peak intensity of anatase increased at 325 °C (f), indicating crystal growth of anatase.

Fig. 4 and 5 show the XRD diffraction patterns of the products obtained by the solvothermal reactions of $H_2Ti_4O_9{\cdot}0.25H_2O$ (a) in methanol and ethanol below 325 °C, respectively. Reaction above 325 °C was not carried out because thermal decomposition of the alcohol became significant.[18] In methanol, $H_2Ti_4O_9{\cdot}0.25H_2O$ is stable up to 250 °C [(b)–(d)], however, it entirely transformed to monoclinic TiO_2 at 280 °C (e). Further, monoclinic TiO_2 partly transformed to anatase at 325 °C (f). It is notable that the formation of $H_2Ti_8O_{17}$ was not observed in methanol and the critical temperature at which anatase appeared was higher than that in water, but lower than that in air. On the other hand, in ethanol, $H_2Ti_4O_9{\cdot}0.25H_2O$ was stable up to 150 °C (b) and both monoclinic TiO_2 and anatase appeared at 200 °C (c). $H_2Ti_4O_9{\cdot}nH_2O$, monoclinic TiO_2 and anatase coexisted in the temperature range 200–325 °C [(c)–(e)]. It is seen that the peak intensity corresponding to anatase of the product in ethanol was stronger than that in methanol at the same temperature.

Microstructure of the product

Scanning electron micrographs of (a) $K_2Ti_4O_9$, (b) $H_2Ti_4O_9{\cdot}0.25H_2O$ and TiO_2 (monoclinic TiO_2, anatase and a mixture of them) prepared by heat treatment of $H_2Ti_4O_9{\cdot}0.25H_2O$ in (c) air at 550 °C, (d) water at 250 °C, (e) methanol at 325 °C and (f) ethanol at 325 °C are shown in Fig. 6. All samples possessed a fibrous structure similar to that of $K_2Ti_4O_9$ which was used as a starting material, however, their microstructures were quite different as shown in Fig. 7. The sample prepared by calcination in air at 550 °C consisted of lightly agglomerated fine particles of monoclinic TiO_2. In contrast, the powders prepared by hydrothermal treatment at

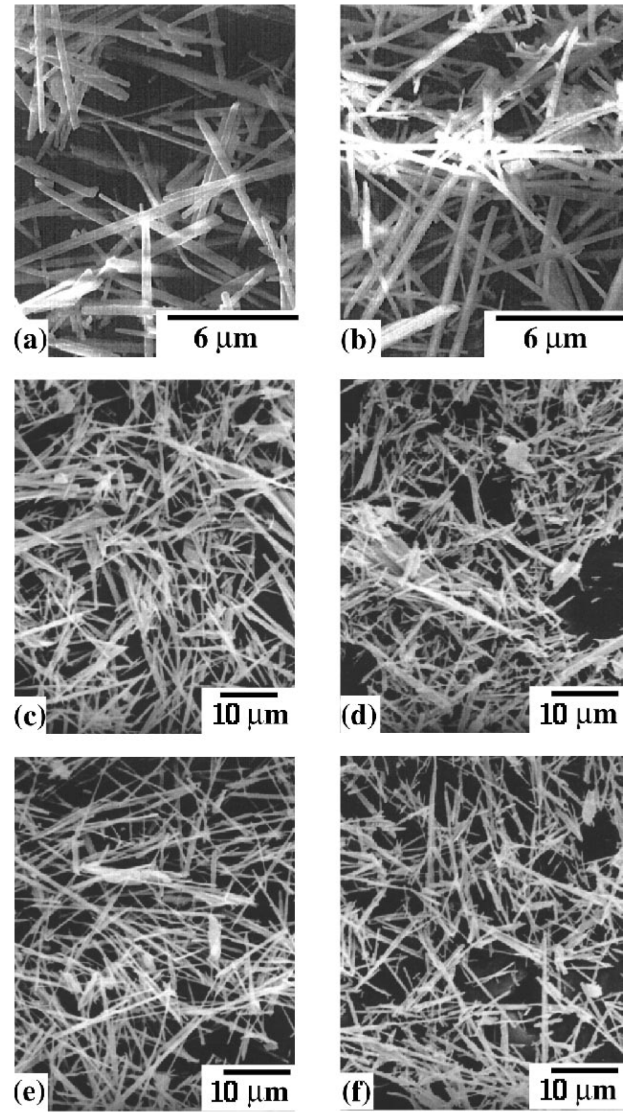

Fig. 6 SEM photographs of $K_2Ti_4O_9$ (a), $H_2Ti_4O_9{\cdot}0.25H_2O$ (b), and products of the heat treatments of $H_2Ti_4O_9{\cdot}0.25H_2O$ in air at 550 °C (c), water at 250 °C (d), methanol at 325 °C (e) and ethanol at 325 °C (f) for 1 h.

250 °C consisted of well crystallised anatase crystals of dimensions 50–100 nm. The powder prepared by solvothermal treatment in ethanol was a mixture of anatase (major) and monoclinic TiO_2 (minor) and consisted of rod-like crystals. On the other hand, the powder prepared by the solvothermal treatment in methanol was a mixture of monoclinic TiO_2 (major) and anatase (minor) and also consisted of rod-like crystals. The crystallite sizes of the products formed in methanol and ethanol were much larger than those produced by calcination in air, but smaller than that by hydrothermal treatment at 250 °C.

Discussion

The phase transformation behaviour of $H_2Ti_4O_9{\cdot}nH_2O$ by heat treatment in air, water, methanol and ethanol is summarized in Fig. 8. It was found that the formation of $H_2Ti_8O_{17}$ was limited to a narrow temperature range of 200–250 °C in air and water, and $H_2Ti_8O_{17}$ was not formed in methanol and ethanol, indicating that the dehydration of $H_2Ti_8O_{17}$ was promoted in alcohols. The critical temperature at which monoclinic TiO_2 appeared did not change significantly, but that at which anatase appeared greatly decreased in liquid media in the order: air $\gg$ methanol $>$ ethanol $>$ water, indicating that the phase transformation of monoclinic TiO_2 to anatase was promoted upon increasing the solubility of titania in the solvent. These results suggested that the phase transformation proceeded by a dissolution–precipitation mechanism.

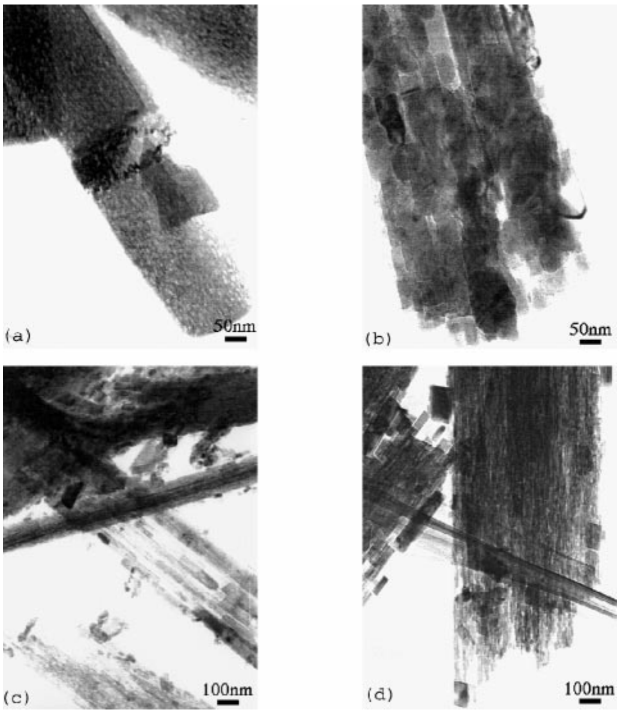

Fig. 7 TEM photographs of titania prepared by the heat treatment of $H_2Ti_4O_9{\cdot}0.25H_2O$ in air at 550 °C (a), water at 250 °C (b), methanol at 325 °C (c) and ethanol at 325 °C (d) for 1 h.

The crystallite sizes of the products also changed significantly, depending on the reaction media (Fig. 7). The crystals formed in methanol and ethanol were much larger than those in air, but smaller than those in water. Probably, this is due to the low solubility of the product in alcohols. These results also suggested that the phase transformation proceeded by a dissolution–reprecipitation mechanism as observed for the crystallisation of amorphous titania and zirconia under solvothermal conditions.[16,17,19]

Conclusions

(1) $H_2Ti_4O_9{\cdot}nH_2O$ prepared by ion exchange reaction of potassium tetratitanate in 1 M HCl at 30 °C for 2 h sequentially transformed to $H_2Ti_8O_{17}$, monoclinic titania, anatase and rutile by heat treatment in air and/or liquid media such as water, methanol and ethanol.

(2) The phase transformation to anatase was promoted by liquid media.

(3) Anatase crystals of 50–100 nm diameter were obtained by hydrothermal treatment of $H_2Ti_4O_9{\cdot}nH_2O$ at 250 °C for 1 h, however, mixtures of monoclinic TiO_2 and anatase were obtained by solvothermal reactions in methanol and ethanol at 325 °C and the crystallite size of the titania could be decreased using alcohol as a reaction medium.

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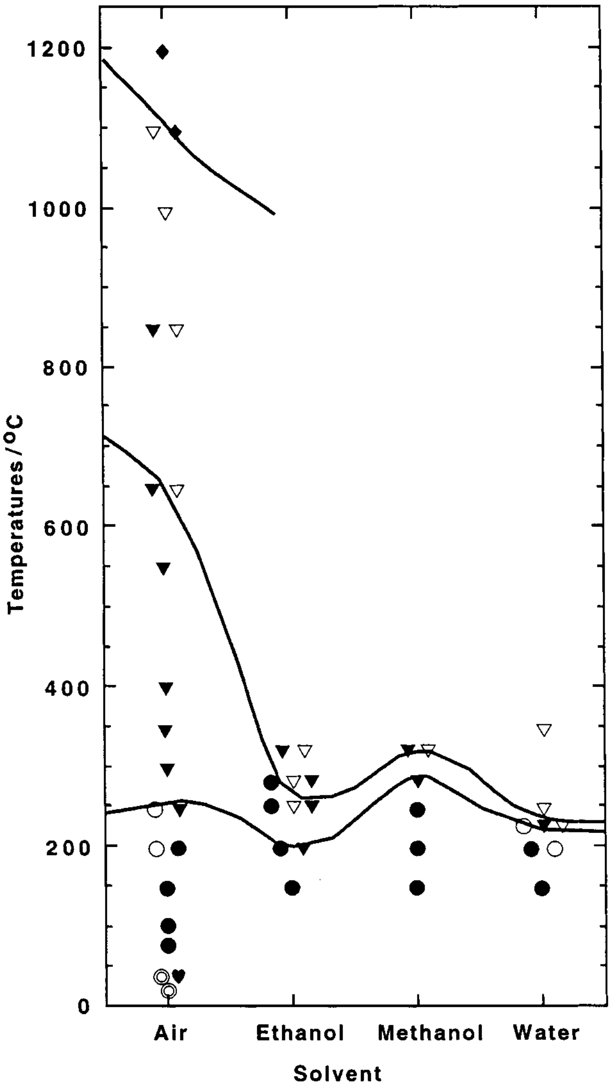

Fig. 8 Phase transformation diagram of $H_2Ti_4O_9{\cdot}nH_2O$ in different reaction media. ◆ Rutile, ▽ anatase, ▼ monoclinic TiO_2, ○ $H_2Ti_8O_{17}$, ● $H_2Ti_4O_9{\cdot}0.25H_2O$, ♥ $H_2Ti_4O_9{\cdot}H_2O$, ◎ $H_2Ti_4O_9{\cdot}1.75H_2O$.

References

1 H. Izawa, S. Kikkawa and M. Koizumi, *J. Phys. Chem.*, 1982, **86**, 5023.
2 T. Sasaki, M. Watanabe, Y. Komatsu and Y. Fujiki, *Inorg. Chem.*, 1985, **24**, 2265.
3 M. Shibata, A. Kudo, A. Tanaka, K. Domen, K. Maruya and T. Onishi, *Chem. Lett.*, 1987, 1017.
4 T. Sato, M. Masaki, T. Yoshioka and A. Okuwaki, *J. Chem. Tech. Biotechnol.*, 1993, **58**, 315.
5 T. Sato, K. Masaki, K. Sato, Y. Fujishiro and A. Okuwaki, *J. Chem. Tech. Biotechnol.*, 1996, **67**, 339.
6 T. Sato, Y. Yamamoto, Y. Fujishiro and S. Uchida, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 5089.
7 S. Uchida, Y. Yamamoto, Y. Fujishiro, A. Watanabe, O. Ito and T. Sato, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 3229.
8 R. Marchand, L. Brohan and M. Tournoux, *Mater. Res. Bull.*, 1980, **15**, 1129.
9 L. Brohan, A. Verbaere and M. Tournoux, *Mater. Res. Bull.*, 1982, **17**, 355.
10 R. Marchand, L. Brohan, R. M'di and M. Tournoux, *Rev. Chim. Miner.*, 1984, **21**, 476.
11 N. Ohta and Y. Fhjiki, *Yogyo-Kyokai-Shi*, 1980, **88**, 1.
12 T. Sasaki, M. Watanabe, Y. Fujiki and Y. Kitami, *Chem. Mater.*, 1994, **6**, 1749.
13 T. Sasaki, S. Nakano, S. Yamauchi and M. Watanabe, *Chem. Mater.*, 1997, **9**, 602.
14 J. F. Banfield, D. R. Veblen and D. J. Smith, *Am. Mineral.*, 1991, **76**, 343.
15 G. Betz, H. Tributsch and R. Marchand, *J. Appl. Electrochem.*, 1984, **14**, 315.
16 S. Yin, Y. Inoue, S. Uchida, Y. Fujishiro and T. Sato, *J. Mater. Res.*, 1998, **13**, 844.
17 Y. Inoue, S. Yin, S. Uchida, M. Ishitsuka, E. Min and T. Sato, *Br. Ceram. Trans.*, 1998, **97**, 222.
18 M. Barj, J. F. Bocquet, K. Chhor and C. Pommier, *J. Mater. Sci.*, 1992, **27**, 2187.
19 T. Sato, Y. Inoue, T. Odashima, M. Ishitsuka and E. Min, *Br. Ceram. Trans.*, 1996, **95**, 99.

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