

Microstructure and crystallization behaviour of TiO₂ precursor prepared by the sol–gel method using metal alkoxide

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TiO₂ precursors were prepared by the sol–gel method using titanium tetraisopropoxide. The effects of water and hydrochloric acid addition for the hydrolysis and polymerization reaction on the crystal lattice or the molecular structure, and on the crystallization behaviour of prepared precursors, were examined by using Raman, and infrared spectroscopy, X-ray diffraction, DTA–TG and carbon analysis. The quantity of unhydrolysed alkyls in precursors decreased with increasing amounts of H₂O and HCl addition, but the alkyls always remained. Raman spectroscopy revealed that the molecular structure of prepared amorphous precursors resembled that of the anatase phase with increased H₂O and HCl addition. On the crystallization process of these precursors, the ratio of anatase formed at 310 °C was influenced by residual unhydrolysed alkyls. Steric hindrance by the residual alkyls preventing crystallization to crystalline anatase was observed, and there was estimated to be 2.5 mol of octahedral coordination of Ti–O per 1 mol of residual alkyls. It is noted that crystallization of the anatase phase and the transformation from anatase to the rutile phase were also observed on long-term ageing of precursors at room temperature.

1. Introduction

The sol–gel method is one of the suitable ways of preparing fine powder, fibres and films of metal oxide glasses or crystalline materials. For preparing crystalline materials, this method includes crystallization and/or transformation processes, because the precursors generally consist of fine particles which are amorphous or crude crystallites. Precursors with various microstructures can be prepared by controlling the hydrolysis reaction and sol–gel conditions, giving various degrees of crystallization and transformation behaviours. The various microstructures enable us to control the transition behaviour of precursors and produce a desirable structure. It should be said that the addition of seeds to precursors or using double alkoxides as a raw material are ways of controlling the microstructure of precursors, so as to obtain ceramics with suitable properties by the sol–gel method [1–3].

TiO₂ with anatase or rutile structure is a well-known material having useful electrochemical, dielectric, electroconductive and optical properties. Many studies on preparing films, fibres and fine powder by the sol–gel method have been reported [4–9]. Although the details have not been clear, it is known that the transition behaviour from amorphous to anatase

phase is influenced by the synthetic conditions. It is very important to clarify the effect of synthetic conditions on the crystallization behaviour of precursors for preparing TiO₂ by the sol–gel method. However, most reports concerning the preparation of TiO₂ by this method have mainly focused on techniques for producing films, fibres and fine powder.

In this study, TiO₂ precursors were prepared under various synthetic conditions by the sol–gel method using metal alkoxides, and the effects of synthetic conditions on the crystal structure, short-range order and crystallization behaviour of these precursors were examined by using powder X-ray diffraction (XRD), infrared spectroscopy (IR), Raman spectroscopy, and differential thermal and thermogravimetric analyses (DTA–TG).

2. Experimental procedure

Titanium tetraisopropoxide (TTIP) was used as a raw material. TTIP (18 ml) was dissolved in a mixed solvent of ethanol (70 ml) and various amount of hydrochloric acid. The molar ratio of HCl to TTIP was varied from 0.05 to 0.90. Distilled water dissolved in ethanol (40 ml) was added to the alkoxide solution at

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the rate of 2 ml min^{-1} to hydrolyse the TTIP. The amount of H_2O was also varied from 2.0 to 9.0 in molar ratio of H_2O to TTIP. All of these operations were done in an N_2 atmosphere. Sol samples formed by the hydrolysis process were aged in closed flasks at 40°C for 6 h in order to hydrolyse the TTIP. After the ageing, these samples were heated at 110°C for 7 h in air to obtain dry gel samples. The dry gel samples with organic solvent removed were used as TiO_2 precursors in this study.

DTA–TG measurements were done in air with a heating rate of 5°C min^{-1} . The IR spectroscopic analysis was conducted with a potassium bromide disc technique. The excitation laser wavelength of Raman spectroscopic analysis was 488 nm and the output power was 90 mW. The laser power was sufficiently low to avoid a change of sample character.

The quantity of residual unhydrolysed alkyls in TiO_2 precursor was examined in order to clarify the degree of TTIP hydrolysis reaction. The amount of the alkyls was estimated by using the carbon content in the TiO_2 precursor. For such a measurement it is necessary to remove the organic solvent from the precursor. Because ethyl alcohol comes to the boil at 78.3°C , the heat treatment at 110°C for 7 h is enough to remove the solvent from the precursor. The heat-treatment temperature is lower than the pyrolysis point, described later, of residual unhydrolysed alkyls.

3. Results

3.1. Crystallization behaviour of precursors

The appearances of TiO_2 precursors prepared by various amounts of H_2O and HCl addition are shown in Fig. 1. The hatched area indicates the region in

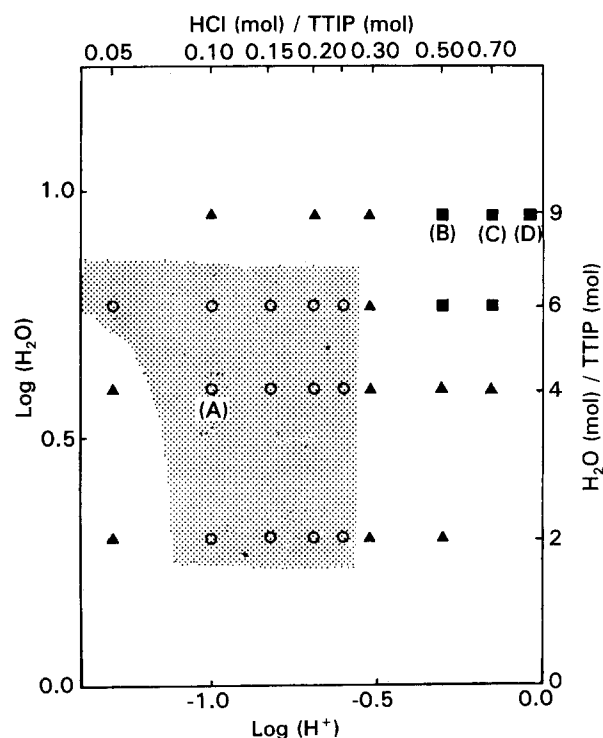


Figure 1 Appearances of dry gel precursors A, B, C and D prepared with various amount of HCl and H_2O additions: (o) clear, (▲) pale white, (■) white.

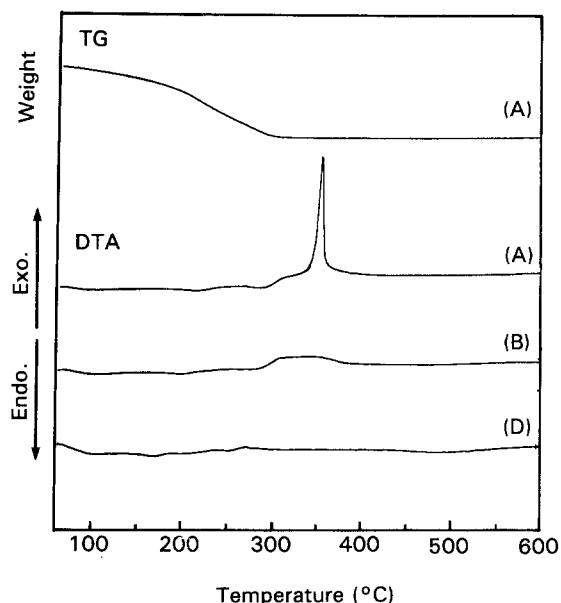


Figure 2 DTA–TG curves of precursors A, B, and D which are the same as those shown in Fig. 1.

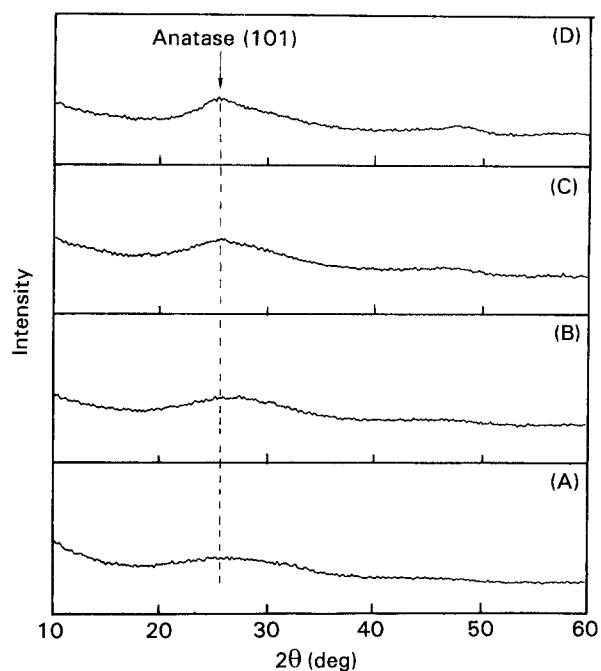


Figure 3 X-ray diffraction patterns of precursors A, B, C and D.

which transparent gel samples were obtained. The conditions for TiO_2 thin film or fibre preparation in previous reports were similar to those in this study [7–9]. When the quantity of H_2O and HCl addition was deficient or excessive, self-condensation occurred and the precursors became opaque and white-coloured.

The crystallization behaviour of precursors prepared under the conditions indicated in Fig. 1 by (A), (B), (C) and (D) is illustrated by typical results in the following figures. Fig. 2 shows DTA curves of the precursors A, B and D and the TG curve of precursor A is also shown in the same figure. Figs 3 and 4 illustrate XRD patterns of these precursors and samples heat-treated at 310°C with a heating rate of

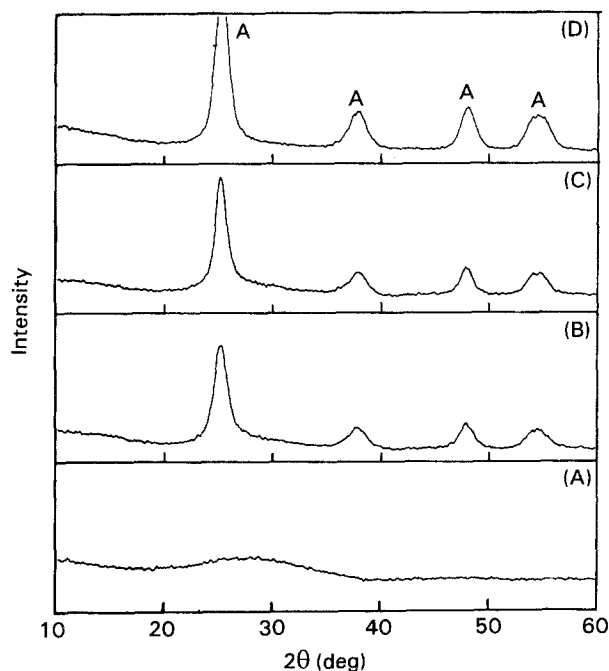


Figure 4 X-ray diffraction patterns of samples A, B, and D after heat treatment at 310°C: anatase peaks are labelled A.

5°C min⁻¹ in air, respectively. All precursors were identified as being in the X-ray amorphous state, although the intensity of the broad peak around a 2θ of 20–25° corresponding to that of the anatase (101) reflection increased with increasing added H₂O and HCl. After the heat treatment at 310°C, samples B, C and D gave XRD patterns of the anatase structure. However, no explicit exothermic peak associated with anatase formation was recognized from the DTA curves shown in Fig. 2. On the other hand, the XRD result for sample A heat-treated at 310°C showed that the sample still remained in the X-ray amorphous state. After heat treatment at a higher temperature (350°C), sample A transformed to the anatase phase. The present result suggests that the exothermic peak at 340°C in the DTA curve of precursor A, which is not associated with weight loss, corresponds to crystallization from the amorphous to the anatase phase. On the TG curve a sudden weight decrease above about 200°C was observed. The transparent precursor A became black and opaque after heat treatment at 310°C, so the sudden decrease of weight was caused by pyrolysis of unhydrolysed alkyls in the precursor structure.

The crystallization to anatase and the transformation behaviour from anatase to rutile were also observed at room temperature by prolonged ageing treatment in air. Fig. 5 illustrates the XRD patterns of precursor D aged for 7 and 200 days at room temperature. Precursor D aged for 7 days, forming anatase, turned to rutile after ageing for 200 days. Both showed broad XRD peaks, indicating that both samples are made of crude crystallites.

3.2. Raman spectra

Raman bands of precursors A, B, C and D are illustrated in Fig. 6. The bands near 1100 cm⁻¹ may be

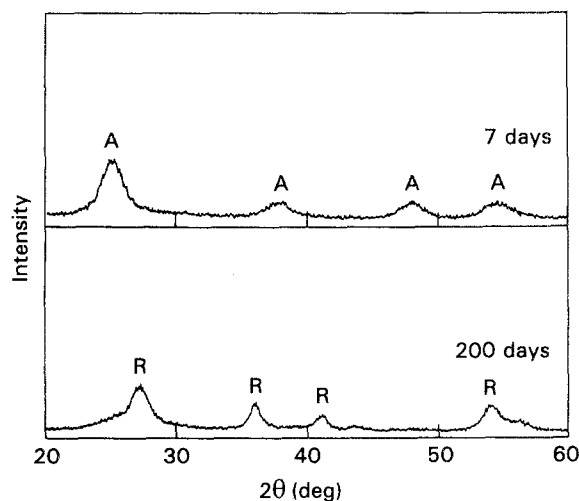


Figure 5 X-ray diffraction patterns of sample D aged for 7 and 200 days at room temperature: (A) anatase, (R) rutile.

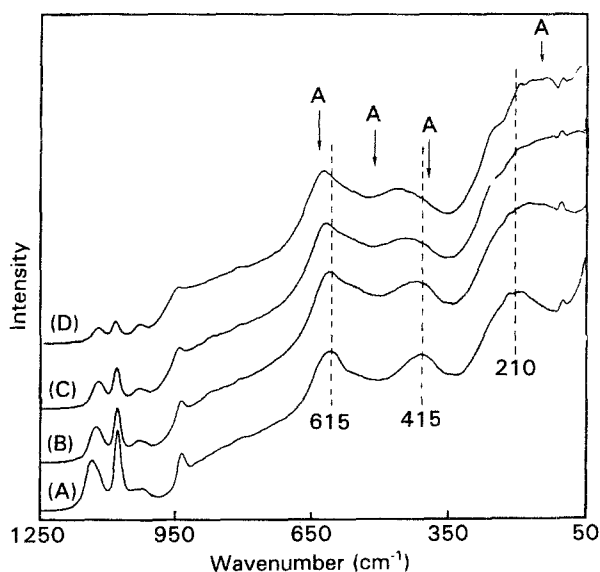


Figure 6 Raman spectra of precursors A, B, C and D: anatase peak positions are labelled A.

associated with residual unhydrolysed alkyls in the precursors. The intensity of these bands became weaker with increasing amounts of HCl and H₂O addition. Broad bands near 415 and 615 cm⁻¹ were observed in all precursors. Ocaña et al. [10] have observed these bands in precursors prepared by the sol-gel method using titanium ethoxide. Exarhors [11] suggested that these bands were identified as being derived from short-range ordered structure in the octahedral coordination of titanium with oxygen, without the long-range order of crystalline anatase or rutile. The broad band at 210 cm⁻¹ was also observed in precursor A, and either second-order scattering or a disorder effect have been suggested to explain its origin [12, 13]. Wave number shifts of bands at 415 and 615 cm⁻¹ were recognized among the precursors A, B, C and D. These bands of precursor D shifted to higher wave numbers and became broader than the others. The band of precursor D near 615 cm⁻¹ showed good coincidence with that of the anatase structure. In addition to this band, an extra broad band around

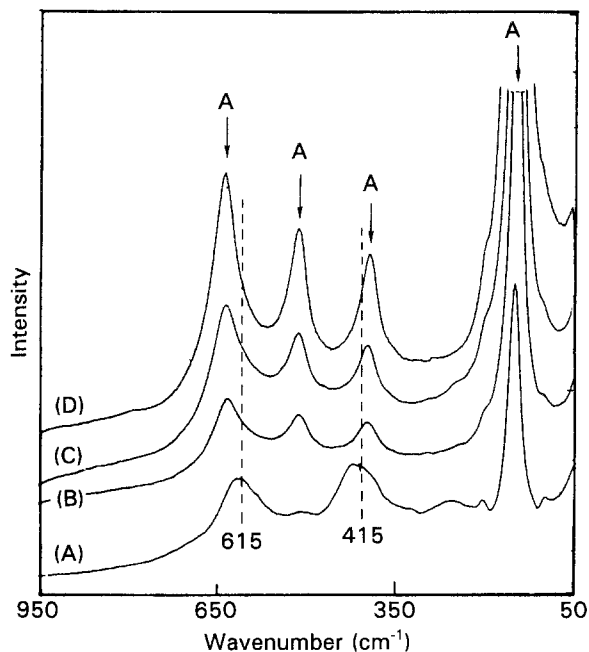


Figure 7 Raman spectra of samples A, B, C and D after heat treatment at 310 °C: anatase peaks are labelled A.

143 cm^{-1} was observed in precursor D. This band was also associated with anatase.

After heat treatment at 310 °C, the bands of anatase at 143, 392, 515 and 635 cm^{-1} shown in Fig. 7 were observed in samples B, C and D which gave the anatase XRD pattern [14]. In particular, the intensity for sample D was stronger than for the others. On the other hand, sample A heat-treated at 310 °C, which gave X-ray amorphous results, showed a band at 143 cm^{-1} for the anatase structure, together with broad bands at 415 and 615 cm^{-1} associated with disordered structure. No changes of wave number in the broad bands at 415 and 615 cm^{-1} were observed between precursor A before and after heat treatment.

3.3. Effect of residual alkyls on crystallization behaviour

The curves in Figs 8 and 9 show the quantitative relations between the residual unhydrolysed alkyls in TiO_2 precursors and the added H_2O and HCl , respectively. The quantity of residual alkyls decreased with increasing amount of added H_2O as shown in Fig. 8. Alkyls remained in the structure for all samples, at more than 0.18 in R/TTIP ratio where R means residual unhydrolysed alkyl group (C_3H_7), even though a large amount of H_2O ($\text{H}_2\text{O}/\text{TTIP} = 20$) was added as shown in Fig. 8. The R/TTIP value of 0.18 means that about one alkyl remains for every six Ti ions on the average.

IR spectra of these precursors are shown in Fig. 10. Absorption bands corresponding to CH_3 were found, and other bands near 1000 cm^{-1} may also be associated with alkyls. The intensity of these absorption bands decreased with increasing amount of added H_2O . The results agreed with the estimates from carbon analysis shown in Fig. 8. These absorption bands of alkyls disappeared owing to pyrolysis when

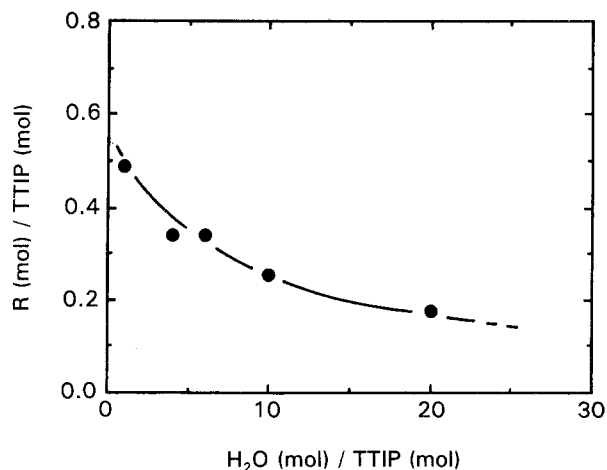


Figure 8 Quantity of residual unhydrolysed alkyls estimated by using carbon analysis in precursors prepared with various amounts of H_2O ($\text{H}_2\text{O}/\text{TTIP} = 1\text{--}20$, $\text{HCl}/\text{TTIP} = 0.15$). Symbols R and TTIP mean residual alkyls and initial charge of titanium tetraisopropoxide, respectively.

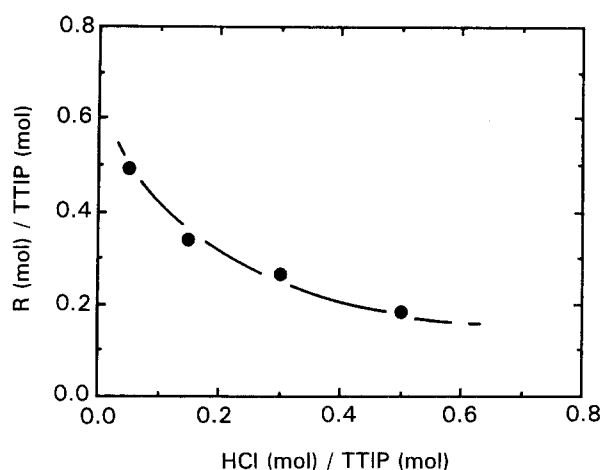


Figure 9 Quantity of residual alkyls in precursors prepared with various amounts of HCl ($\text{HCl}/\text{TTIP} = 0.05\text{--}0.50$, $\text{H}_2\text{O}/\text{TTIP} = 6$).

the precursors were heated at 350 °C. In the case of addition of HCl , as shown in Fig. 9, the quantity of alkyls also decreased with increasing amount of HCl addition, but alkyls always remained at more than 0.18 in R/TTIP ratio.

The relation between the quantity of residual unhydrolysed alkyls in TiO_2 precursors and the volume fraction of anatase formed from the precursors after heat treatment at 320 °C is shown in Fig. 11. The temperature of the heat treatment (320 °C) was lower than that of the exothermic peak of the DTA curve shown in Fig. 2 by 20 °C. When the quantity of residual alkyls was smaller than $\text{TTIP}/R = 2.5$, no anatase phase was observed. Above $\text{TTIP}/R = 3.0$, the volume fraction of anatase formed at 320 °C increased with decreasing residual alkyls in the precursors.

4. Discussion

It has been reported that a transparent TiO_2 gel can be prepared by the addition of HCl which acts as a preventive agent of precipitation and self-condensation of particulate materials [7]. The addition of a

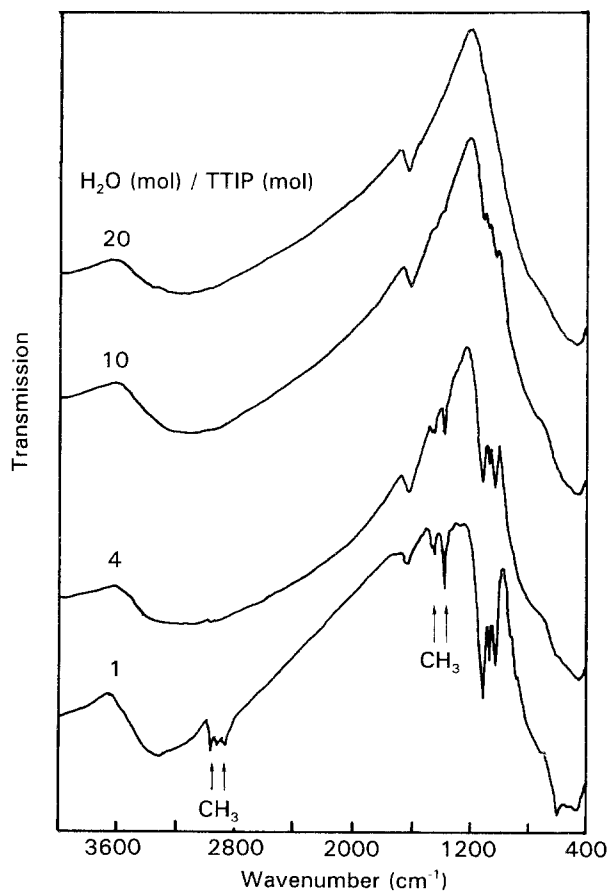


Figure 10 Infrared spectra of precursors which are the same as those prepared with various amounts of H₂O (H₂O/TTIP = 1–20, HCl/TTIP = 0.15) as shown in Fig. 8.

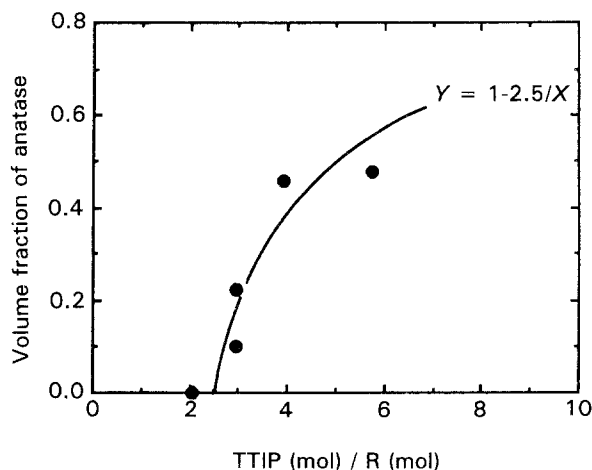
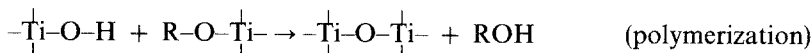
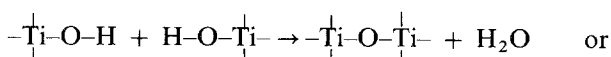
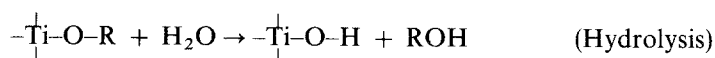


Figure 11 Relation between quantity of residual alkyls in the dry gel precursors and volume fraction of anatase phase formed after heat treatment at 320°C.

large amount of HCl, however, induces precipitation and self-condensation. This may be caused by the considerable change of pH value which influences the stability of particulate materials in solution.

If the hydrolysis and polymerization reactions proceeded as follows:



the hydrolysis and the polymerization reactions are promoted by increasing H₂O addition, and a quantity of added H₂O higher than 2 in H₂O/TTIP ratio should be enough to hydrolyse TTIP completely. In this study the hydrolysis reaction, therefore, proceeded with increasing H₂O addition. However, the results showed that a certain amount of alkyls still remained in precursors prepared with a large amount of H₂O addition. This suggests a steric hindrance in the hydrolysis reaction in which the formed polymer or particulate surrounds unhydrolysed alkyls group with increasing degree of hydrolysis. Yoldas [7] also supposed that the amount of added H₂O influenced the average molecular size and the nature of the terminal bonds in TiO₂ precursors, and that a certain concentration of unreacted alkyls always remained. An increase of HCl addition also leads to a decrease of the amount of residual alkyls. It is possible to give two explanations for the role of HCl. One involves a catalytic role of HCl in the hydrolysis reaction, and the other that of a modifier of the formed polymer structure which influences the degree of hydrolysis reaction. They are, however, inconclusive at this moment.

The Raman results suggest that the short-range structure of precursors is influenced by the amount of both H₂O and HCl additions, although all precursors are X-ray amorphous. When the amounts of H₂O and HCl are small the structure is in a disordered state, but a short-range ordered structure made of octahedral coordination of Ti–O is formed. On the other hand, when the amounts of H₂O and HCl become large the structure resembles that of the anatase phase, although there remains an absence of long-range order. These Raman results suggest that the anatase phase is more stable than the amorphous phase in low-pH solutions.

The volume of anatase phase formed at 320°C increased with decreasing amount of residual unhydrolysed alkyls in the precursors, but no anatase phase was observed below TTIP/R = 2.5 as shown in Fig. 11. Furthermore, no shift was observed between the Raman bands of precursor A and sample A heated at 310°C. This result suggests that octahedral coordination of Ti–O in precursor A does not change during the heating. Therefore, 1 mol of residual unhydrolysed alkyls prevents 2.5 mol of adjoining octahedral coordination of Ti–O from participating in crystallization. This assumption leads to the relation between the volume fraction (*V*) of anatase formed at 320°C and TTIP/R ratio as $V = 1 - 2.5/(\text{TTIP}/\text{R})$ for TTIP/R > 2.5. The curve calculated by using the equation is illustrated in Fig. 11. It shows good agreement with the measured values. The results of DTA–TG and XRD show that the disordered struc-

ture of precursor A with octahedral coordination of Ti–O crystallizes to anatase at around 340 °C, due to pyrolysis of the alkyls which prevented crystallization. On the other hand, when the amount of H₂O and HCl addition is large, the amount of residual alkyls preventing the reconstruction of Ti–O octahedra is small, so the microstructure resembles that of the anatase phase which is more stable than the amorphous phase, and it transforms to the anatase phase at a relative low temperature.

It is interesting to note that the formation of anatase and rutile phases is observed from samples aged for a long time at room temperature. This suggests that the reconstruction of Ti–O octahedra for these transitions and the hydrolysis reaction of residual alkyls preventing the crystallization occur even at room temperature, although the rates of these reactions are very slow. These results suggest that the rutile structure is the most stable in the low-pH solution.

Conclusions

The microstructure and crystallization behaviour of TiO₂ precursors are found to be very influenced by synthetic conditions. The quantity of residual unhydrolysed alkyls in the precursors decreases with increasing amount of H₂O or HCl addition, but more than a certain quantity of the alkyls always remains. The microstructure of amorphous precursors approaches the structure of anatase with increasing H₂O and HCl addition. On the crystallization to anatase formed at 320 °C, the residual alkyls influence the volume fraction of anatase phase formed at 320 °C. It is plausible to conclude that 1 mol of alkyls prevents 2.5 mol of adjoining octahedral coordination of Ti–O from taking part in the transition. The crystallization

of anatase and the transformation from anatase to rutile are also observed at room temperature by long-term ageing.

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References

1. H. DISLICH, *Angew. Chem. Internat. Edit.* **10** (1971) 363.
2. R. ROY, *Science* **238** (1987) 1664.
3. M. KUMAGAI and G. MESSING, *J. Amer. Ceram. Soc.* **68** (1985) 500.
4. E. A. BARRINGER and H. K. BOWEN, *ibid.* **65** (1982) C199.
5. T. IKEMOTO, K. UEMATSU, N. MIZUTANI and M. KATO, *Yogyo-Kyokai-shi* **93** (1985) 55.
6. K. KATO, in "Ceramic Transactions", Vol. 22 (Ceramic Powder Science–IV) (American Ceramic Society, Westerville, Ohio, 1991) p. 63.
7. B. E. YOLDAS, *J. Mater. Sci.* **21** (1986) 1087.
8. K. KAMIYA, K. TANIMOTO and T. YOKO, *J. Mater. Sci. Lett.* **5** (1986) 402.
9. T. YOKO, K. KAMIYA and S. SAKKA, *Yogyo-Kyokai-shi* **95** (1987) 12.
10. M. OCAÑA, J. V. GARCIA-RAMOS and C. J. SERNA, *J. Amer. Ceram. Soc.* **75** (1992) 2010.
11. G. J. EXARHOS, *J. Vac. Soc. Technol. A* **4** (1986) 2962.
12. M. OCAÑA, V. FORNES, J. V. GARCIA RAMOS and C. J. SERNA, *J. Solid State Chem.* **75** (1988) 364.
13. C. A. MELENDRES, A. NARAYANASWAMY, V. A. MARONI and R. W. SIEGEL, *J. Mater. Res.* **4** (1989) 1246.
14. A. TURKOVIĆ, M. INANDA, A. DRAŠNER, V. VRAN-EŠA and M. PERŠIN, *Thin Solid Films* **198** (1991) 199.

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