

Synthesis and intercalation properties of nanoscale layered tetratitanate

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Received 25th October 2001, Accepted 8th April 2002

First published as an Advance Article on the web 30th April 2002

Nanoscale layered tetratitanate $K_2Ti_4O_9$ powders were prepared at relatively low temperature by a stearic acid method. The structures of the titanates and the products which had undergone H^+ , Ag^+ exchange and intercalated by propylamine and $NH_2(CH_2)_3Si(OC_2H_5)_3$ (APS) were investigated by XRD, TEM, TG and BET analysis. Compared with the larger-size products prepared by a conventional solid state reaction, the nanoscale $K_2Ti_4O_9$ takes in more intercalating molecules and leads to larger interlayer distances in the intercalated products, which may facilitate the exfoliation of the layered compound.

Introduction

Peculiar properties differing from bulk materials may appear as the dimensions of a materials are reduced to the submicrometer or nanometre scale.¹ Study of the preparation and properties of various nanostructured materials has received extensive attention during the last two decades.¹ In this article, we report a novel method to synthesize ultrafine layered titanate ($K_2Ti_4O_9$) and some new exchange and intercalation properties of this material.

The layered titanate compounds (e.g. $Na_2Ti_3O_7$, $K_2Ti_4O_9$, $CsTi_2NbO_7$, $KTiNbO_5$) have been studied extensively as ion exchangers,^{2–6} metal ion adsorbents^{7,8} and fillers in reinforced plastics.^{9–11} Various nanocomposites may be formed *via* the intercalation of new species (e.g. CdS, PbS, Fe_2O_3 , TiO_2 , SiO_2 , Al_2O_3 and porphyrin) into the interlayer space for photocatalysis applications.^{12–19} The exfoliated nanosheets of these compounds have also been used as building blocks to construct self-assembled multilayers and to produce nanotubes.^{20,21} However, the actual particle size of these compounds was usually at least on the micrometer scale because they were usually prepared *via* a solid state reaction of TiO_2 with K_2CO_3 at high temperatures (800–1300 °C) with long reaction times.^{12–19,22} Because of the difficulty in preparing ultrafine layered titanates by the conventional solid-state reaction, little attention has been paid to investigating the change of the structure and properties of these compounds when the particle size of these compounds becomes smaller.

One of the typical strategies to synthesize nanoscale complex oxides is using precursor routes.²³ We previously developed an organic precursor route to synthesize nanocrystalline complex oxides using melted stearic acid as a dispersant.^{24–26} It was found that various metallic ions could be dispersed at the molecular level in melted stearic acid *via* a liquid state mixing process, and each component was uniformly mixed even in the resulting product after removing organic substances by combustion. This could remarkably reduce the solid state reaction temperature and ultrafine complex oxides could be easily obtained. Herein, we used this method to synthesize a nanoscale layered tetratitanate ($K_2Ti_4O_9$).

Experimental

Synthesis

Tetrabutyltitanate ($Ti(O-Bu)_4$) and KOH were used as the precursors in our experiment. Stearic acid was used as the solvent and dispersant. The molar ratio of $Ti(O-Bu)_4$, KOH

and stearic acid was 1.75:1:4. Excess KOH was used to account for losses due to volatilization at high temperature. Firstly, an appropriate amount of stearic acid was heated and melted in a beaker at 90–120 °C, into which KOH saturated solution was added. This mixture was kept at 90–120 °C and thoroughly stirred by a magnetic heating mixer to eliminate the water. Then the $Ti(O-Bu)_4$ was added while stirring vigorously. After two hours, a homogenous transparent solution was formed. The solution was poured into an alumina crucible and heated in a furnace in air to ~300 °C. At this temperature, the solution was ignited and the obtained powders were calcined at various temperatures for 2.5 h. The product obtained at 800 °C was further used for H^+ exchanging. For comparison, $K_2Ti_4O_9$ powders were also prepared by a conventional solid state reaction. A stoichiometric mixture of K_2CO_3 and TiO_2 was heated at various temperatures and the products obtained at 1080 °C for 6 h were further used in intercalation reactions. In the following description, the prefixes (S- and C-) are used to identify the $K_2Ti_4O_9$ samples (and their derivatives) prepared by the stearic acid route and the conventional solid-state reaction, respectively.

The protonated $K_2Ti_4O_9$ (denoted as H-Ti) was obtained by exchanging K^+ of $K_2Ti_4O_9$ (ca. 1 g) in 1000 mL of 1 M HCl at 60 °C for 3 days. The acid solution was renewed every day in order to remove K^+ completely from the compounds. The products were washed with distilled water and dried in vacuum at 30 °C. n-Propylamine ($C_3H_7NH_2$) was incorporated between the layers of H-Ti (products denoted as amine-Ti) by dispersing 1 g H-Ti powders into 50 ml 20 vol% of $C_3H_7NH_2$ aqueous solutions and stirring at 60 °C for 3 days. The solid material was separated by centrifugation and further dried in vacuum at 30 °C.

To intercalate $NH_2(CH_2)_3Si(OC_2H_5)_3$ (APS), 0.5 g n-propylamine intercalated titanates were mixed with 10 wt% aqueous solution of APS (Si:Ti = 13:3). The mixture was refluxed for 24 hours, followed by centrifuging and washing with distilled water. The obtained products (APS-Ti) were dried in vacuum at 50 °C, and further calcined at 400 °C to obtain SiO_2 -pillared tetratitanates (SiO_2 -Ti).¹³ Ag^+ was exchanged into the interlayers of H-Ti by stirring H-Ti in 0.06 M $AgNO_3$ solution for 3 days, followed by washing with distilled water and drying at 30 °C in air.

Characterization

X-Ray powder diffraction (XRD) patterns were collected on a Bruker D8 ADVANCE diffractometer with $Cu-K\alpha$ radiation

($\lambda = 0.15405$ nm). Transmission electron microscopy (TEM) was performed with an H-800 microscope using 175 kV acceleration voltage. The BET specific surface area of samples was obtained by nitrogen adsorption/desorption isotherms at liquid nitrogen temperature (77 K) using a Micromeritics ASAP 2010C instrument.

The products were further characterized by chemical analysis, which was carried out as follows. The products were dissolved in concentrated sulfuric acid and ammonium sulfate with heating. The potassium content in the products was determined by atomic absorption spectrophotometry. The water content in the interlayer was deduced by measuring the weight loss at 800 °C using thermogravimetric (TG) analysis,^{3,27} which was carried out with a Shimadzu TGA-50 thermogravimetric analyzer at a heating rate of 10 °C min⁻¹ under air atmosphere. The propylamine content was deduced by TG and CHN analysis which was carried out with a CE-440 analyzer.

Results and discussion

The XRD patterns of the powders prepared by different methods are shown in Figs. 1 and 2. For the stearic acid route, the products calcined at < 750 °C were mainly amorphous (see XRD patterns in Fig. 1a and 1b). The XRD pattern shown in Fig. 1c is in good agreement with that of K₂Ti₄O₉ (JCPDS 32-0861),²² indicating that crystallized K₂Ti₄O₉ was formed at 750 °C. However, for the conventional solid state reaction, no K₂Ti₄O₉ phase was detected in the product calcined at 750 °C (Fig. 2a). Only the phases of unreacted TiO₂ and K₂Ti₆O₁₃ (JCPDS 40-0403) were identified. When the products were calcined at 800 °C, K₂Ti₄O₉ and K₂Ti₆O₁₃ coexisted. K₂Ti₆O₁₃ disappeared only after calcination at 1080 °C for 6 hours (see Fig. 2c). These results indicate that K₂Ti₄O₉ crystallites could be obtained at lower temperature using this stearic acid method.

Fig. 3 shows the TEM photographs of the resulting S-K₂Ti₄O₉ and C-K₂Ti₄O₉ powders. Compared with the products prepared by the conventional solid state reaction, the resulting S-K₂Ti₄O₉ particles are also whisker-like, but with much smaller whisker size than that of C-K₂Ti₄O₉ (about 5 micrometers long and 500 nanometers wide). The length of these whiskers is in the range from 100 nm to 1000 nm with a relatively wide distribution, while the width of most whiskers is approximately 50 nm. The lower reaction temperature may lead to the formation of smaller K₂Ti₄O₉ powders.

As shown in Figs. 1 and 2, the XRD pattern of S-K₂Ti₄O₉ powder is identical to that of C-K₂Ti₄O₉ powder, indicating that their crystal structures are the same. The chemical analysis

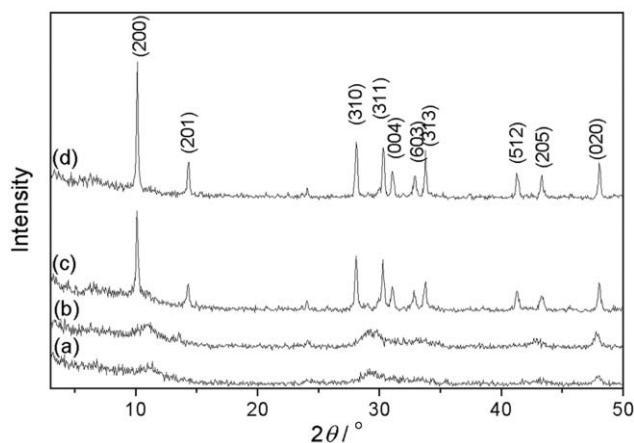


Fig. 1 XRD patterns of the samples prepared by the stearic acid method at various temperatures for 2.5 h: (a) 500 °C; (b) 700 °C; (c) 750 °C; (d) 800 °C.

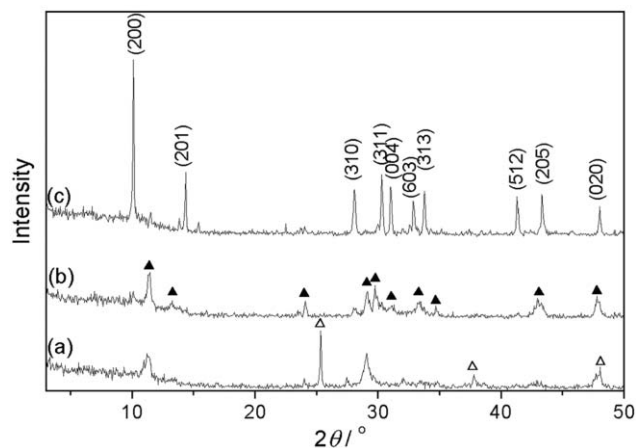


Fig. 2 XRD patterns of samples prepared by conventional solid state reaction calcined at various temperatures: (a) 750 °C, 2.5 h; (b) 800 °C, 2.5 h; (c) 1080 °C, 6 h (▲: K₂Ti₆O₁₃ △: TiO₂).

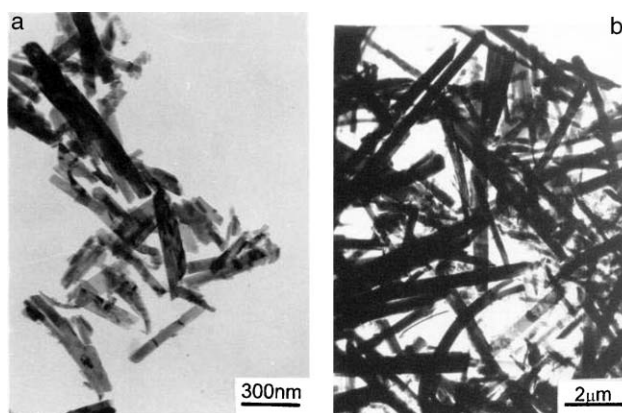


Fig. 3 TEM images of S-K₂Ti₄O₉ (a) and C-K₂Ti₄O₉ (b).

of the samples shows that the chemical compositions of both S-K₂Ti₄O₉ and C-K₂Ti₄O₉ are also almost identical and their H⁺ exchanged products contain only a negligible amount of potassium (see Table 1). However, the XRD patterns of their H⁺-exchanged products were different (see Fig. 4a and 4b). The pattern of C-H-Ti is in agreement with the data reported in ref. 27. But in the pattern of S-H-Ti, the *d*(200) value is much larger than that of C-H-Ti, which indicates that the interlayer distance of S-H-Ti is larger than that of C-H-Ti.

TG analysis results of C-H-Ti and S-H-Ti are shown in Fig. 5(a, b). According to ref. 27, the weight loss below 120 °C represents the release of the interlayer water, so the calculated numbers of interlayer water molecules of S-H-Ti and C-H-Ti are approximately 1.40 and 0.33 respectively, which imply that more water molecules were intercalated into the interlayer of S-H-Ti. This may account for the different *d*(200) values in the XRD profiles.

Similar to the H⁺ exchanged products, their propylamine incorporated products also showed some differences. Fig. 5c and 5d are the TG curves of the newly prepared S-amine-Ti and C-amine-Ti samples. They exhibited three distinct mass loss steps: the first (below 120 °C) was due to the loss of physical absorbed water and propylamine molecules; The second mass

Table 1 Chemical analysis results of some samples

Content (mass%)	S-K ₂ Ti ₄ O ₉	C-K ₂ Ti ₄ O ₉	S-H-Ti	C-H-Ti
K	18.9	19.0	0.15	0.20
Ti	46.20	45.70	52.76	55.73

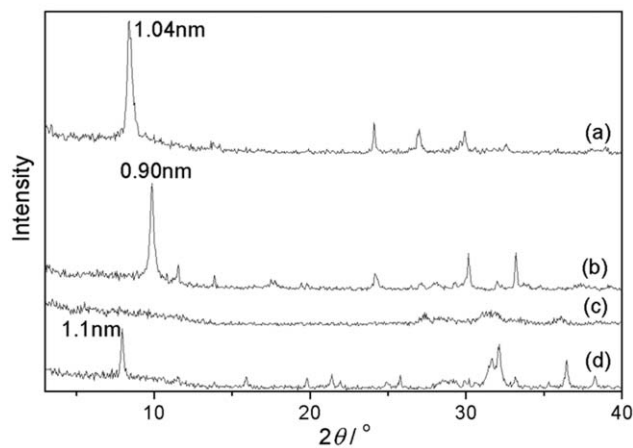


Fig. 4 XRD patterns of (a) S-H-Ti; (b) C-H-Ti; (c) S-Ag⁺-Ti; (d) C-Ag⁺-Ti.

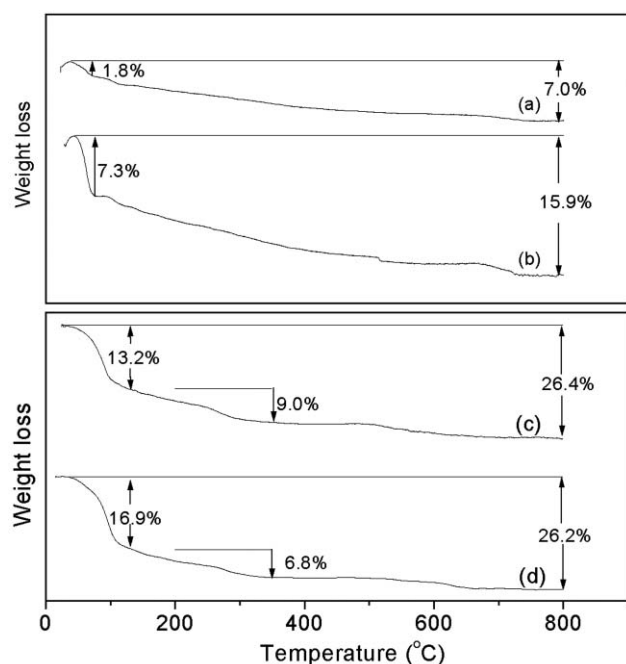


Fig. 5 TG of H-Ti and amine-Ti samples: (a) C-H-Ti; (b) S-H-Ti; (c) C-amine-Ti; (d) S-amine-Ti.

loss step (120–350 °C) was attributed to the decomposition of interlayer propylamine molecules, and the last one corresponds to the loss of lattice water molecules.²⁸ Based on the TG and CHN results (shown in Table 2), the propylamine contents absorbed on the surface and intercalated in the interlayer may be evaluated and the results are also shown in Table 2.^{29,30} It was found that the amount of intercalated propylamine in S-amine-Ti was more than that in C-amine-Ti. We repeated the preparation of amine-Ti three times and the TG, CHN analyses always showed consistent results.

Fig. 6 shows the XRD patterns of the propylamine-incorporated products, which also exhibit a little difference. The interlayer distance of S-amine-Ti is slightly larger than that of C-amine-Ti. This may also be caused by the difference of the contents of incorporated propylamine.

The XRD patterns of the APS-incorporated samples are shown in Fig. 7. It can be seen that the $d(200)$ of S-APS-Ti is 2.1 nm, which is also larger than that of C-APS-Ti (1.9 nm), indicating that more APS was intercalated into S-amine-Ti. Even after calcination at 400 °C, the difference is still maintained. In recent years, SiO₂ and other oxide pillared titanates

Table 2 Carbon (C) and nitrogen (N) elemental analysis results of the amine-Ti samples and the calculated propylamine distribution based on CHN and TG analysis

Sample	C (%)	N (%)	Content of propylamine absorbed on the surface (mol%)	Content of propylamine intercalated in the interlayer (mol%)
S-amine-Ti	8.20	3.24	0.39	0.66
C-amine-Ti	9.67	3.97	0.85	0.38

have received interest due to their potential applications in catalysis.^{12–17} Yanagisawa *et al.* reported that the microstructure of TiO₂-pillared H₂Ti₄O₉ could be controlled by the length of the alkylamines prior to expansion.²⁹ Our result implies that the structure of pillared titanates might also be tailored by controlling the size of the host layered oxides.

Besides the influence of particle size on intercalation ability, we found that the particle size also affected the exfoliation ability. The XRD patterns of the Ag⁺-exchanged H-Ti powders are shown in Fig. 4c–4d. The laminar structure of C-H-Ti still remained and $d(200)$ was increased to 1.1 nm after treatment with AgNO₃ solution. However, as for S-H-Ti, the $d(200)$ peak almost disappeared after being Ag⁺-exchanged, which indicated that the layered structure was exfoliated or at least partially exfoliated.³¹

The experimental results described above clearly indicate

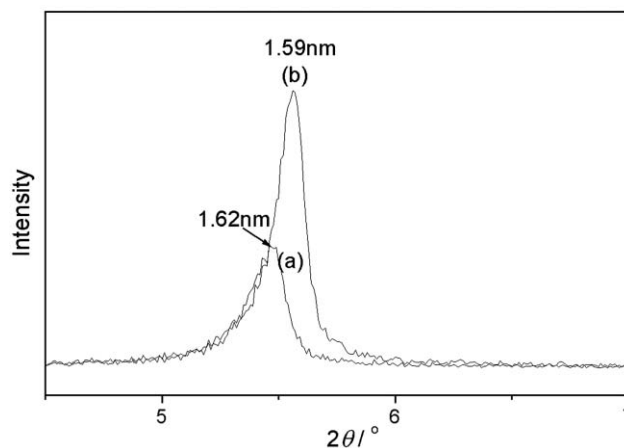


Fig. 6 XRD patterns of n-propylamine incorporated products: (a) S-amine-Ti; (b) C-amine-Ti.

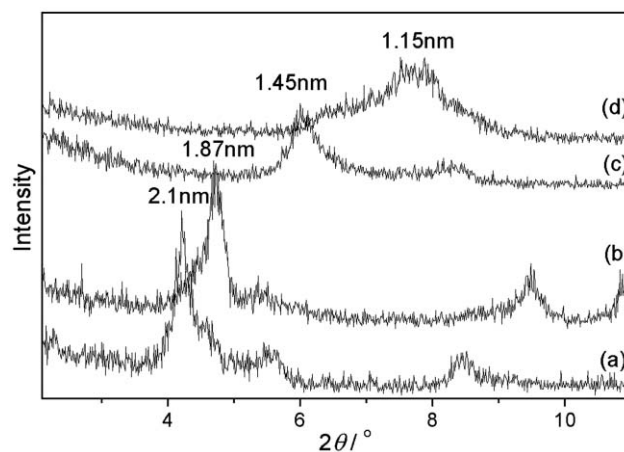


Fig. 7 XRD patterns of APS incorporated products (a) S-APS-Ti; (b) C-APS-Ti and after calcination at 400 °C for 2.5 h; (c) S-SiO₂-Ti; (d) C-SiO₂-Ti.

that the particle size of $K_2Ti_4O_9$ does affect the intercalation and exfoliation of the layered compound. However, the exact mechanism is not clear yet. Possibly, we supposed that the small S- $K_2Ti_4O_9$ particles might have greater crystalline defects, which may decrease the interlayer charge density and weaken the interaction between TiO_6 octahedral layers.

Besides $K_2Ti_4O_9$, the intercalation and exfoliation of other layered compounds with interlayer exchangeable ions like smectite,^{32,33} layered double hydroxides^{34,35} and some other titanates and niobates^{36–38} have also received considerable attention in recent years. Several methods have been developed to improve the delamination ability of layered compounds by controlling the chemical composition of the layered hosts or choosing appropriate delamination agents and solvents. Our experiment may provide another approach to facilitate the intercalation/delamination reactions, which are useful for the preparation of new nanostructures.

In addition, the decrease of the particle size of layered titanates will lead to the increase of their surface area, which will improve catalytic activity. Recently, Hayashi *et al.*³⁹ found that RuO_2 supported $K_2Ti_6O_{13}$ prepared by a hydrothermal method had a higher surface area and higher photocatalytic activity than that prepared by a conventional solid state reaction. We also found that $K_2Ti_4O_9$ prepared by the stearic acid method (S- $K_2Ti_4O_9$) has a much higher specific surface area ($44.7\text{ m}^2\text{ g}^{-1}$) than C- $K_2Ti_4O_9$ ($9.3\text{ m}^2\text{ g}^{-1}$). Because of the simplicity of the stearic acid route, it is expected that this method can also be used for preparation of high activity catalysts.

Conclusion

Nanoscale $K_2Ti_4O_9$ powders were prepared at low temperature using a stearic acid precursor. Compared with the products synthesized by the conventional solid state reaction, nanoscale $K_2Ti_4O_9$ powders exhibit the same crystal structure but with different ions exchanged and APS intercalated products. These results suggested that the properties of layered compounds might be size dependent and it may be a new way to improve the intercalation or exfoliation ability of layered compounds by decreasing their particle size.

Acknowledgement

The authors are grateful for the financial support of Doctoral and Postdoctoral Foundation of the Ministry of Education of P. R. China and Postdoctoral Foundation of China.

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