

Preparation of ultrafine layered tetratitanate powders using nanoscale TiO_2 as reactant and their intercalation property

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Ultrafine layered potassium tetratitanate $\text{K}_2\text{Ti}_4\text{O}_9$ powders were prepared by solid-state reaction using nanometer sized TiO_2 as the reactant. The structures of the titanates and the products which had undergone H^+ exchange and intercalated by propylamine and $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ (Al_{13}^{7+}) were investigated by XRD, TEM, TG and BET analysis. Compared with the larger-sized products prepared by using micrometer sized TiO_2 , the ultrafine $\text{K}_2\text{Ti}_4\text{O}_9$ takes in more intercalating molecules, which leads to the expanding of the interlayer distance of the resulting products. The final Al_2O_3 pillared ultrafine tetratitanate exhibits higher BET surface area ($212.8 \text{ cm}^2 \text{ g}^{-1}$) and narrow pore-size distribution.

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1. Introduction

A number of layered inorganic solids have received considerable attention in recent years because of their unique structures and chemical reactivity [1–8]. Particularly the intercalation property of layered materials has been extensively studied. Various nanocomposites have been formed via the intercalation of new species into the interlayer space and this provides a useful strategy to create novel porous materials and inorganic/organic nanocomposites [9, 10]. It has been reported that the introduction of small semiconducting particles of CdS-ZnS, Fe_2O_3 and TiO_2 into the interlayer of layered materials such as montmorillonite, smectite clays, layered niobate and layered titanate gives rise to a remarkable enhancement of their photocatalytic activity compared with unsupported catalyst [9, 11–13].

Behaving as semiconductors, layered titanates have been extensively studied due to their applications in photocatalysts and catalyst supports [14, 15]. But the intercalation of layered titanates are not easy to achieve since these types of layered materials do not possess swelling ability due to their high charge density [16]. Intercalation of large species into the titanates can be achieved by a templating technique in which the interlayer spacing of the protonic titanates is pre-expanded with long alkylamine chains [16–18]. New methods are being explored to improve the intercalation property of layered titanates [16, 19].

It is known that the properties of materials may be influenced by the sizes and peculiar properties differing from bulk materials may appear as the dimension of materials is reduced to the submicrometer or nanometer scale [20]. For layered materials, Leroux suggested that the charge density might be influenced by the specific

surface areas, in another word, by the particle size of the materials [21]. Our recent research does indicate that the exchange/intercalation property of $\text{K}_2\text{Ti}_4\text{O}_9$ is extensively influenced by its particle size and nanoscaled $\text{K}_2\text{Ti}_4\text{O}_9$ prepared by stearic acid precursor route facilitates the chemical reaction in the interlayer space [22]. But compared with the conventional solid-state method, the stearic acid route is too costly and can be used only for laboratory preparation.

According to our experience in preparing nanostructured complex oxides via solid state reaction, decreasing reaction temperature and shortening reaction time favor the formation of smaller products. It is well known that this can be realized by decreasing the size of the reactants. So we supposed that the particle sizes of layered titanates might be controlled by the particle size of the reactants. Using nanoscale raw materials, ultrafine or nanostructured products may be obtained. Based on this concept, ultrafine layered $\text{K}_2\text{Ti}_4\text{O}_9$ powders were successfully prepared in this report via conventional solid-state reaction simply by decreasing the particle size of raw material TiO_2 and it was found that the intercalation property of $\text{K}_2\text{Ti}_4\text{O}_9$ is strongly dependent on the particle size of the layered compound.

2. Experimental

Anatase titanium dioxide powders with different average particle sizes (their TEM images showed the average particle sizes were approximately 20 nm and $>1 \mu\text{m}$ respectively) and K_2CO_3 with analytical purity were used as the raw materials.

$\text{K}_2\text{Ti}_4\text{O}_9(\text{I})$ powders were prepared by heating a mixture of K_2CO_3 and TiO_2 (20 nm) in a molar ratio of 1:3.5

at 800°C for 60 h. For comparison, $K_2Ti_4O_9$ (II) powders were obtained by heating the mixture of K_2CO_3 and TiO_2 ($>1 \mu m$) in a molar ratio of 1:3.3 at 1080°C for 6 h. The excess K_2CO_3 was used to account for the loss due to volatilization at high temperature.

The protonated form of $K_2Ti_4O_9$, $H_2Ti_4O_9 \cdot nH_2O$ (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 everyday 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 inside the layer 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.

To intercalate Al^{7+} , 0.5 g *n*-propylamine intercalated titanates were mixed with 25 mL $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (Al^{7+}) solution which was prepared as follows: The *n*-propylamine was added dropwise to $AlCl_3$ solution (the final *n*-propylamine/Al mole ratio was 2.5) with vigorous stirring and the final pH value was adjusted to 4–4.5. The resultant mixture was heated with stirring at 50°C for 8 h, followed by centrifuging and washing with distilled water. The obtained products (Al^{7+} -Ti) were dried in vacuum at 50°C and further calcined at 500°C to obtain alumina-pillared tetratitanates (Al_2O_3 -Ti).

X-ray powder diffraction (XRD) patterns were collected on a Bruker D8 ADVANCE diffractometer with Cu-K α 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 Micromeritics ASAP 2010C instrument.

The chemical composition of the obtained tetratitanate, the water content in the interlayer of H-Ti and the propylamine content in the interlayer of amine-Ti were deduced by the same manner described in Ref. [22].

3. Results and discussion

The solid-state reaction was studied by the XRD experiment and the results are shown in Figs 1 and 2. In the reaction system of (20 nm) TiO_2 and K_2CO_3 , $K_2Ti_4O_9$ (JCPDS 32-0861) [23] and the intermediate phase $K_2Ti_6O_{13}$ (JCPDS 40-0403) coexisted during the calcination process (Fig. 1a and b) and pure $K_2Ti_4O_9$ was obtained after the mixture calcined at 800°C for 30 h (Fig. 1c). However, in the system of ($>1 \mu m$) TiO_2 , a mass of $K_2Ti_6O_{13}$ phase still existed when the mixture was calcined at 800°C for 30 h (Fig. 2c), and pure $K_2Ti_4O_9$ could only be obtained after the mixture was further calcined at 1080°C for 6 h (Fig. 2d).

Fig. 3 shows the TEM photographs of the resulting $K_2Ti_4O_9$ powders. The two samples are both whisker-like but with different sizes. The $K_2Ti_4O_9$ (II) particles are about 5 micrometers long and 500 nanometers wide while $K_2Ti_4O_9$ (I) shows much smaller whisker size. The length of these whiskers is in the range of from 200

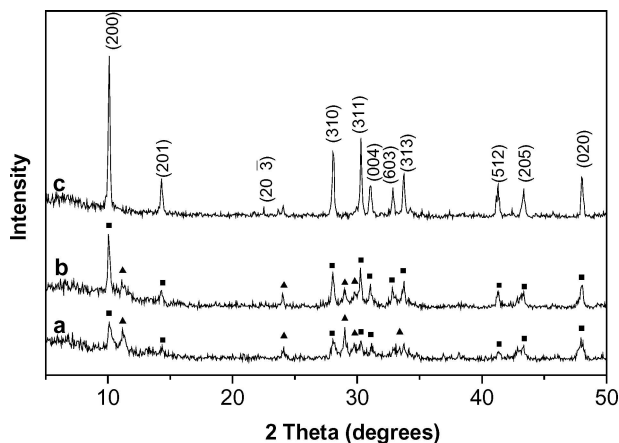


Figure 1 XRD patterns of the mixture of TiO_2 (20 nm) with K_2CO_3 calcined at 800°C for different time: (a) 2.5 h; (b) 6 h; (c) 30 h. (■: $K_2Ti_4O_9$; ▲: $K_2Ti_6O_{13}$).

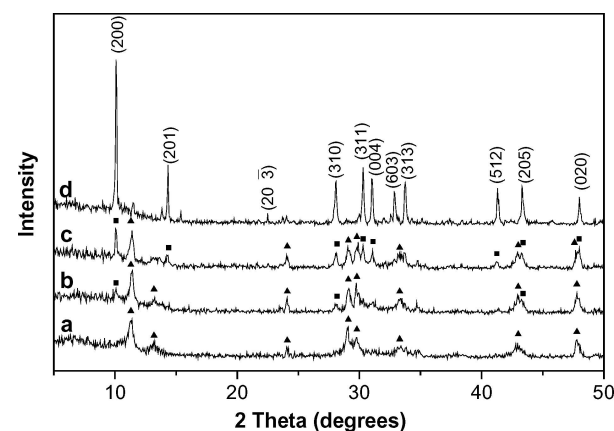


Figure 2 XRD patterns of the mixture of TiO_2 ($>1 \mu m$) with K_2CO_3 calcined at different conditions: (a) 800°C 2.5 h; (b) 800°C 6 h; (c) 800°C 30 h; (d) 1080°C 6 h. (■: $K_2Ti_4O_9$; ▲: $K_2Ti_6O_{13}$).

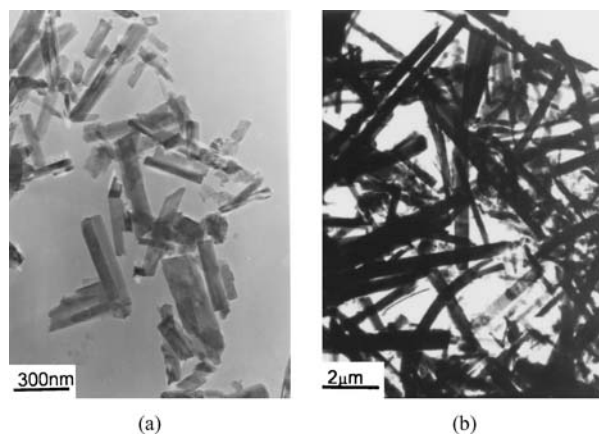


Figure 3 TEM micrographs of (a) $K_2Ti_4O_9$ (I) and (b) $K_2Ti_4O_9$ (II) samples.

to 600 nm with a relatively wide distribution, while the width of most whiskers is approximately 70 nm. The higher reaction rate and lower reaction temperature may lead to the formation of smaller $K_2Ti_4O_9$ powders.

As shown in Figs 1 and 2, the XRD patterns of the ultimate two $K_2Ti_4O_9$ samples are almost the same and are in agreement with the data reported in Ref. [23], which indicates that the final crystal structure of the

TABLE I Chemical analysis results and lattice parameters of $K_2Ti_4O_9$ and its protonic exchanged products (30°C)

	Chemical analysis		Lattice parameters			
	Content of K (mass%)	Content of Ti (mass%)	a (Å)	b (Å)	c (Å)	β (deg)
$K_2Ti_4O_9$ (I)	19.0	45.95	18.16	3.77	11.96	106.34
$K_2Ti_4O_9$ (II)	19.3	45.70	17.95	3.73	11.81	106.33
H-Ti(I)	0.19	53.01	23.19	3.87	11.0	106.6
H-Ti(II)	0.20	55.73	18.99	3.79	11.69	104.8

samples is not influenced by the particle size of the reactants in the solid state reaction. The chemical analysis results shown in Table I also imply that the chemical composition of the two samples is almost the same. But the XRD patterns of their H^+ -exchanged products are different (see Fig. 4a and b). The pattern of H-Ti(II) is in agreement with the data reported in Ref. [23]. But in the pattern of H-Ti(I), $d(200)$ value is larger than that of H-Ti(II), which indicates that the interlayer distance of H-Ti(I) is larger than that of H-Ti(II). According to the chemical analysis shown in Table I, the H-Ti products are confirmed to contain a negligible amount of potassium ions (<2.0 mg/g material). TG results of H-Ti(I) and H-Ti(II) are shown in Fig. 5a and b. According to the TG analysis described in Ref. [22], the interlayer

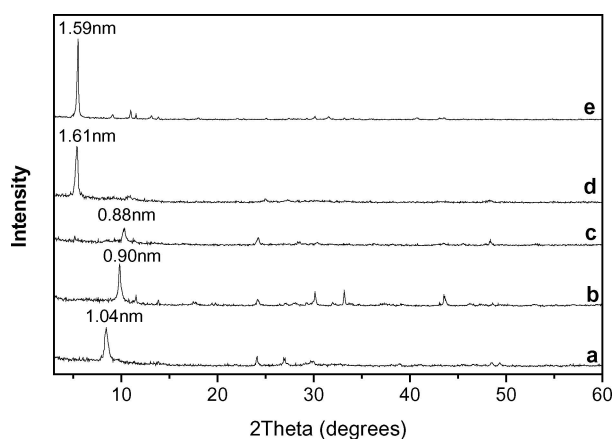


Figure 4 XRD patterns of (a) H-Ti(I) 30°C, (b) H-Ti(II) 30°C, (c) H-Ti(I) 50°C, (d) amine-Ti(I) and (e) amine-Ti(II).

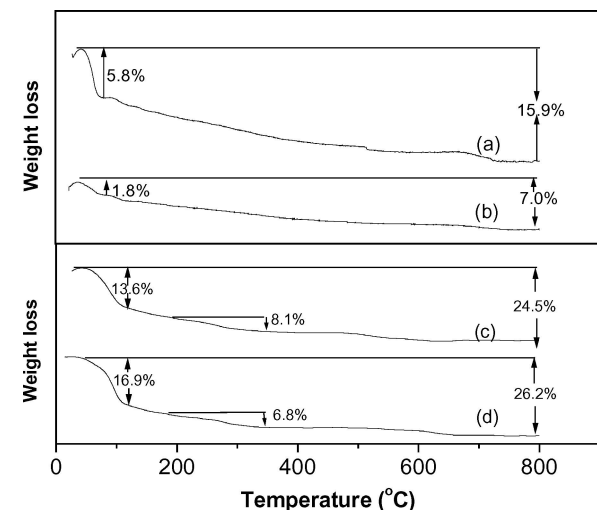


Figure 5 TG of H-Ti and amine-Ti samples: (a) H-Ti(I); (b) H-Ti(II); (c) amine-Ti(I); (d) amine-Ti(II).

water molecules of H-Ti(I) and H-Ti(II) are approximately 1.26 mol and 0.33 mol per formula weight respectively, which implies that more water molecules were intercalated into the interlayer of H-Ti(I). This result is also confirmed by the XRD pattern of H-Ti(I) sample further dried in vacuum at 50°C (Fig. 4c), the $d(200)$ value decreased to 0.88 nm indicating that the interlayer water was partially evaporated.

The crystal structure of $K_2Ti_4O_9$ is monoclinic and the lattice parameters of samples $K_2Ti_4O_9$ and $H_2Ti_4O_9 \cdot nH_2O$ are listed in Table I. The lattice parameters of the two $K_2Ti_4O_9$ samples are almost the same indicating that the crystal structure is not influenced by the particle size of the reactants in the solid state reaction. After the H^+ -exchanging, the unit cell a parameter increased but b , c , β parameters changed little, which suggested that the expanding of the interlayer distance was probably due to the exchange of K^+ for H_3O^+ without changing of the host Ti_4O_9 layers (1). The a parameter of H-Ti(I) is larger than that of H-Ti(II), and this can also confirm the XRD and TG analysis that more H_2O molecules are existing in the interlayer of H-Ti(I).

Similar to the H^+ exchanged products, their propylamine incorporated products also showed some differences. XRD patterns of the propylamine-incorporated products are shown in Fig. 4d and e. The interlayer distance of amine-Ti(I) is also a little larger than that of amine-Ti(II). After the TG analysis (Fig. 5c and d) together with the CHN elemental analysis (methods described in Ref. [22], results listed in Table II), it was found that the amount of intercalated propylamine in amine-Ti(I) (48 mol%) was more than that in the amine-Ti(II) (38 mol%), which might lead to the differences of the XRD patterns.

XRD patterns of the Al_{13}^{7+} -incorporated samples are shown in Fig. 6a and b. It can be seen that the $d(200)$ of Al_{13}^{7+} -Ti(I) is 1.81 nm, which is little smaller than that of Al_{13}^{7+} -Ti(II) (1.91 nm) and this result is not in agreement with those in H-Ti and amine-Ti samples. We repeated the preparation of Al_{13}^{7+} -Ti three times and

TABLE II Carbon (C) and Nitrogen (N) elemental analysis results of the amine-Ti samples and the calculated propylamine distribution based on the TG and CHN results

Sample	C(%)	N(%)	Content of propylamine absorbed on the surface (mol%)	Content of propylamine intercalated in the interlayer (mol%)
H-Ti(I)	9.34	3.83	68	48
H-Ti(II)	9.67	3.97	85	38

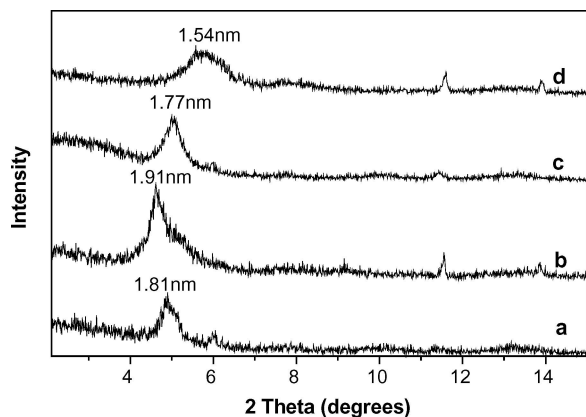


Figure 6 XRD patterns of Al_{13}^{7+} incorporated samples (a) Al_{13}^{7+} -Ti(I); (b) Al_{13}^{7+} -Ti(II) and after calcined at 200°C for 2.5 h (c) (I); (d) (II).

the XRD analyses always showed consistent results. According to Nawla [20], the interlayer charge density of layered compounds will be decreased by the intercalation of Al_{13}^{7+} . So we considered that this difference might be caused by the small size effect of the titanate together with the function of the interlayer Al_{13}^{7+} , and the exact mechanism was still in progress. Fig. 6c and d are the XRD patterns of the Al_{13}^{7+} -Ti samples further calcined at 200°C for 2 h. It is found that $d(200)$ of sample(I) is 1.77 nm, which is larger than that of sample(II) (1.54 nm), indicating that more Al_{13}^{7+} might be intercalated into sample(I). And for sample(II), a small peak appeared at about 11.5° . Although we are not so sure of the mechanism causing the difference between the two Al_{13}^{7+} intercalating samples at present time, but it does indicate that the intercalation property of the layered titanate is influenced by the particle size and this may further affect the microstructure of the intercalated products.

After heat-treated at 500°C for 2 h, the interlayer Al_{13}^{7+} was decomposed into Al_2O_3 [24]. Results of the N_2 adsorption/desorption experiments are shown in Fig. 7. It can be seen that pore structure of the Al_2O_3 -Ti is extensively influenced by the particle size of the layered titanate and this may further influence their surface areas. In fact, the BET surface area of Al_2O_3 -Ti(I)

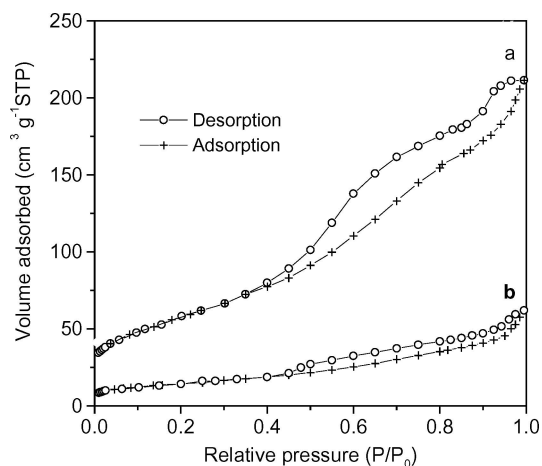


Figure 7 Nitrogen adsorption-desorption isotherms of (a) Al_2O_3 -Ti(I) and (b) Al_2O_3 -Ti(II).

is $212.8 \text{ m}^2 \text{ g}^{-1}$, much larger than that of Al_2O_3 -Ti(II), $53.0 \text{ m}^2 \text{ g}^{-1}$. High surface area is attractive in its applications such as catalysts and catalysts supports. Recently, Yanagisawa etc. [15] reported that the surface area of titania-pillared tetratitanate can be controlled by the lengths of alkylamine, and high surface area can be obtained by using alkylamine with long chains such as $\text{C}_{18}\text{H}_{37}\text{NH}_2$ as the pre-intercalation agent. Our experimental results herein suggest that the pillared tetratitanate with high specific surface area can also be obtained by using nanoscaled titanate as the host material.

The experimental results described above clearly indicated that the ability of intercalation of layered compounds might be improved through reducing their particle size. However, the exact mechanism is not clear yet. Possibly, we supposed that the ultrafine $\text{K}_2\text{Ti}_4\text{O}_9$ might have higher crystalline defects, which may decrease the interlayer charge density and weaken the interaction between Ti-O octahedral layers. Further study of this area may be of interest.

4. Conclusions

Ultrafine $\text{K}_2\text{Ti}_4\text{O}_9$ powders were prepared at relatively low temperature via solid-state reaction using nanometer sized TiO_2 as the reactant. Compared with the larger products, ultrafine $\text{K}_2\text{Ti}_4\text{O}_9$ powders exhibit the same crystal structure but with different ions exchanged and Al_{13}^{7+} intercalated products. Al_2O_3 pillared tetratitanate with high specific surface area is obtained by using the ultrafine $\text{K}_2\text{Ti}_4\text{O}_9$ as the host material. These results suggested that the properties of layered compounds might be dependent on the particle size of starting materials for preparing those layered compounds.

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