

# Thermal analysis of hydrogen titanate nanotubes prepared by potassium dititanate with water vapour treatment

Yujiao Xie · Chang Liu · Hanbing He · Xiaohua Lu

Received: 19 June 2011 / Accepted: 5 September 2011 / Published online: 18 September 2011  
© Akadémiai Kiadó, Budapest, Hungary 2011

**Abstract** Hydrogen titanate nanotubes were prepared by  $K_2Ti_2O_5$  with water vapour treatment. TG/DTG techniques were used to investigate their water content and dehydration kinetics. It was shown that chemical formula for hydrogen titanate nanotubes is  $TiO_2 \cdot 0.58H_2O$  which is close to  $H_2Ti_2O_5$ . The activation energy of dehydration from hydrogen titanate nanotubes is about 60 kJ/mol according the calculation of Friedman and Flynn–Wall–Ozawa methods. With multivariate non-linear regression calculation, it was found that dehydration of hydrogen titanate nanotubes is a two-step consecutive reaction. The first step is a reaction of  $n$ th order with autocatalysis. The second step is a reaction of  $n$ th order.

**Keywords** Potassium dititanate · Titanate nanotubes · Chemical formula · Dehydration kinetics

## Introduction

Protonated titanate nanotubes synthesized by the hydrothermal method have become the target of many studies in recent years because of its unique combination of physicochemical and structural properties [1]. Nanotubular titanates can be potentially utilized in a wide range of applications, including catalysis, photocatalysis, hydrogen storage, lithium batteries and solar cells [2]. Since their discovery by Kasuga et al. in 1998 [3], much effort has been spent to understand the mechanism of nanotubular

titanate formation, allowing control of the morphology of nanotubes via the adjustment of the synthesis conditions [4, 5].

However, the crystalline structure and formation mechanism of titanate nanotubes are still topics under discussion. Kasuga et al. [3] concluded that titania nanotubes were produced after hydrothermal reaction and washing the alkali-treated specimen with water followed by a further treatment with HCl. Zhang et al. [6] found that the structure of the tubular materials do not agree with those made of  $TiO_2$  crystals with either anatase or rutile phase, but are similar to that of layered titanate  $H_2Ti_3O_7$  according to detailed electron and X-ray diffraction studies. Recently, Yang et al. investigated the composition and structure of this nanotube material and found that it is nanotube  $Na_2Ti_2O_4(OH)_2$ , which can be converted to nanotube  $H_2Ti_2O_4(OH)_2$  in a pH 1 HCl solution, and its crystalline form belongs to an orthorhombic system. They indicated that the intensities of the deformation and stretching vibrations of water at 1,630 and 3,400  $cm^{-1}$  decreased to constant values in IR spectra at  $t > 6$  h during vacuum drying at room temperature [7]. Sun and Li [8] also studied the formation mechanism of titanate nanotubes, and demonstrated the existence of large amounts of water and hydroxy groups in the titanate nanotubes. Thus, it is interesting and important to investigate interaction between  $H_2O$ , hydroxyl group and  $TiO_6$  units in titanate nanotube. To the best of our knowledge, there is no report on study of the dehydration behaviour of titanate nanotube with thermal analysis technologies.

In our recent work [9, 10], a new soft-chemistry approach was developed to prepare hydrogen titanate nanotubes. Layered titanate- $K_2Ti_2O_5$  was used as precursor and treated with water vapour. After removing potassium ion in acid solution, hydrogen titanate nanotubes were

Y. Xie · C. Liu · H. He · X. Lu (✉)  
State Key Laboratory of Materials-Oriented Chemical  
Engineering, Nanjing University of Technology,  
Nanjing 210009, China  
e-mail: xhlu@njut.edu.cn

formed. If  $K_2Ti_2O_5$  was washed with acid solution without water vapour treatment, hydrogen titanate nanoribbons will be formed. This process is suitable for large scale preparation due to the short reaction time, low temperature and high yield. In this article, thermal analysis technologies will be used to investigate dehydration behaviour for the hydrogen titanate nanotubes and nanoribbons.

## Experimental

The procedure for hydrogen titanate nanotubes is as follows: (1) the calcination of  $TiO_2$  with  $K_2CO_3$  to form  $K_2Ti_2O_5$ ; (2) treatment of  $K_2Ti_2O_5$  by water vapour (141.325 kPa, 109.6 °C) for 3 h; (3) ion exchange of  $K^+$  to  $H^+$  in 0.1 M HCl solution, then samples were washed with deionized water until  $pH = 7$ , and dried in oven at 60 °C. Finally, hydrogen titanate nanotube bundles are formed. This sample was labelled as S1. In comparison, potassium dititanate was washed with 0.1 M HCl and deionized water directly. After drying at 60 °C, sample was labelled as S2.

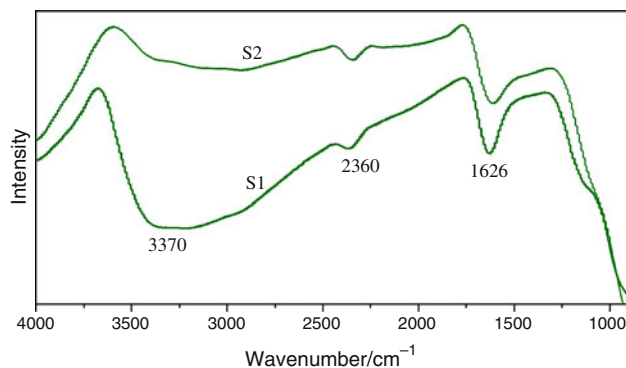
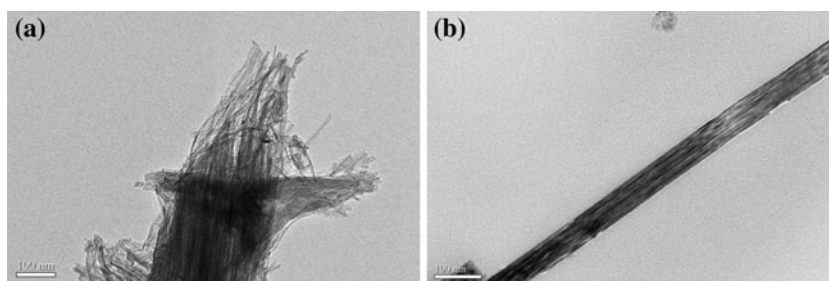
TEM images were obtained with a JEOL JEM-200CX transmission electron microscope operating at 200 kV. FTIR spectra of the samples were recorded by Nicolet 6,700 spectrometer. Simultaneous TG–DTG measurements were carried out on a Netzsch TG209 F3 thermal analyzer. The thermal analysis was performed in nitrogen, at heating rates of 5, 10, 15 and 20 °C/min. The mass was kept at  $6.50 \pm 0.15$  mg. Thermokinetics software was used for kinetics analysis.

## Results and discussion

### TEM results

Figure 1 shows TEM pictures for sample S1 and S2. It can be found that sample S1 is nanotube bundles. The outer and inner diameter of these nanotubes is about 4 and 10 nm, respectively. However, sample S2 shows nanoribbon morphology with diameter of 100 nm. It indicates that the structure of sample S1 is looser than that of sample S2.

**Fig. 1** TEM images for sample S1 (a) and sample S2 (b)



**Fig. 2** FTIR spectra of hydrogen titanate nanotubes (S1) and nanoribbons (S2)

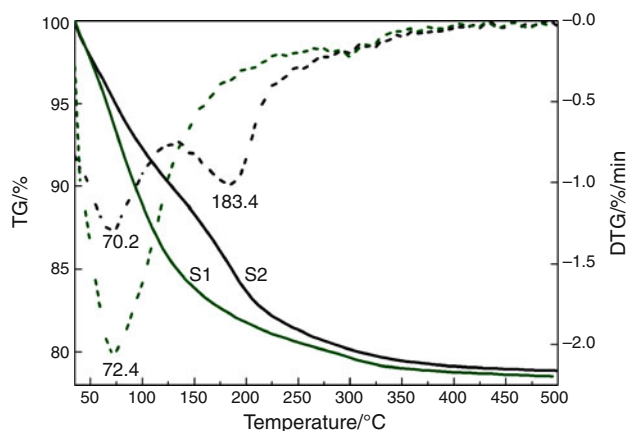
### Fourier transform infrared spectroscopy (FTIR)

Generally, the FTIR spectra is used to investigate the water and hydroxyl groups vibration [7, 8]. As shown in Fig. 2, the FTIR spectra of S2 has peaks at about 3,300 and 1,626  $cm^{-1}$ , which are due to the vibration of adsorbed water and hydroxyl groups, respectively. While S1 has a more prominent peak at about 3,370  $cm^{-1}$ . In our previous work, it was found that the strong interaction exist between water and  $TiO_2$  surface. The residence time of water at  $TiO_2$  surface is considerably longer than that at graphite surface by molecular dynamics simulations [11]. Compared with S2, we inferred that some bound water or hydroxyl groups exist besides the adsorbed water in titanate nanotubes.

### TG/DTG analysis

Figure 3 shows the dehydration process of sample S1 and S2 at heating rate of 10 °C/min in nitrogen atmosphere. Sample S1 and S2 show nearly the same mass loss 26.82% at 30–500 °C in TG curves. If a chemical formula  $TiO_2 \cdot nH_2O$  is used to represent hydrogen titanate nanotubes and nanoribbons, the value of  $n$  can be calculated from the mass loss and is 1.2.

While DTG curves for the two samples show obvious difference. There are two stages of mass loss with peaks at



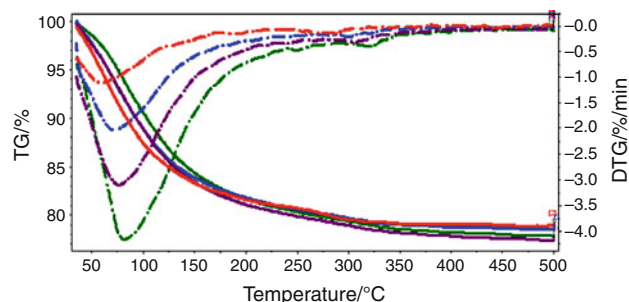
**Fig. 3** TG and DTG curves of sample *S1* and sample *S2* heating at 10 °C/min in nitrogen atmosphere

**Table 1** Mass changes of dehydration of *S1* and *S2*

Mass change step	Temperature range/°C	Mass loss/%	Chemical formula
<i>S1</i>			
1	35–100	11.13	TiO <sub>2</sub> ·0.58H <sub>2</sub> O
2	100–500	10.35	
<i>S2</i>			
1	35–135	10.51	TiO <sub>2</sub> ·0.60H <sub>2</sub> O
2	135–500	10.62	

70.2 and 183.4 °C in DTG curve of *S2*. The first stage is from 35 to 135 °C, with a mass loss of 10.51%. It is attributed to the loss of free water, and the second stage (135–500 °C) has a mass loss of 10.62% due to the dehydration of crystal water. However, there is only a stage for water loss with a peak at 72.4 °C from 35 to 500 °C in DTG curve of *S1*. At this condition, it is difficult to distinguish free water and crystal water in sample *S1*. Yang et al. [12] investigated dehydration of H<sub>2</sub>Ti<sub>5</sub>O<sub>11</sub>·H<sub>2</sub>O and assumed that free water could be evaporated up to 100 °C. With the same assumption, the dehydration of sample *S1* was analyzed and results are listed in Table 1.

It is clear that water vapour treatment has a significant effect on morphologies of final products and water bonded status on them, although the crystal water content in both samples are almost the same which was shown in Table 1. The empirical chemical formula for hydrogen titanate nanotubes is TiO<sub>2</sub>·0.58H<sub>2</sub>O. Compared with two different chemical formula for hydrogen titanate nanotubes appeared in papers H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> (which can be written as TiO<sub>2</sub>·0.33H<sub>2</sub>O) and H<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub> (which can be written as TiO<sub>2</sub>·0.5H<sub>2</sub>O), we believe that hydrogen titanate nanotubes is probably H<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub> and accompanied with some bound water.



**Fig. 4** TG and DTG curves of dehydration of *S1* (heating rate 5, 10, 15, 20 °C/min)

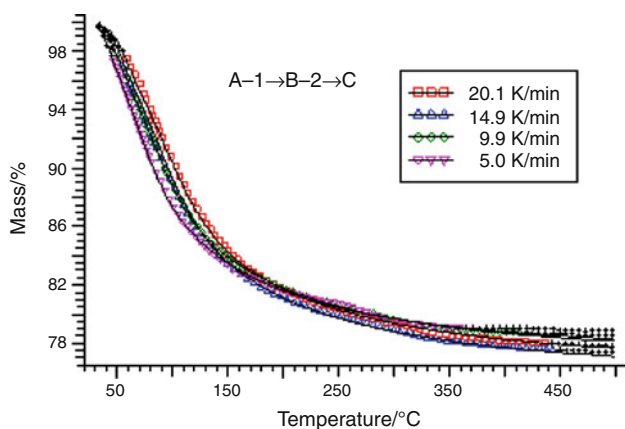
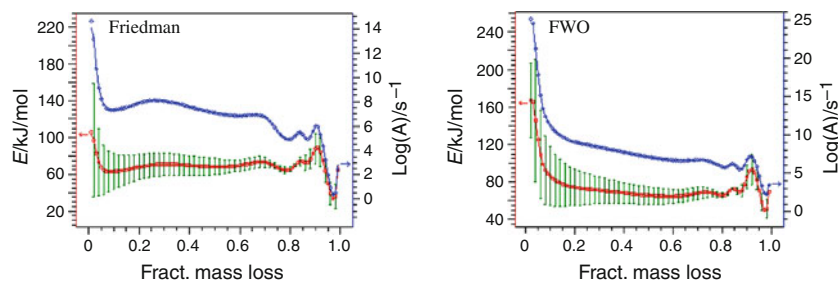
### Kinetic analysis of dehydration

The TG and DTG curves of sample *S1* with different heating rates are shown in Fig. 4. At first, the model-free approaches, Friedman [13] and Flynn–Wall–Ozawa (FWO) methods [14, 15] were used to investigate the kinetics parameters of dehydration process. The two methods are based on multiple heating rate experiments and can be used for obtaining activation energy, where no kinetic model is needed [16, 17].

Figure 5 shows that the apparent activation energies and pre-exponential factor of dehydration of *S1* calculated with Friedman and FWO method. The curves exhibit the same shape, and the little differences could be explained by considering the relations which ground the isoconversional methods [18–20]. In the range  $0.01 < a < 0.1$ , the activation energy decreased from a large initial value down to the normal ones, which suggests there is a reversible reaction in the beginning of the dehydration. While in the range of  $0.1 < a < 0.7$ , the activation energy has a practically constant value, 60 kJ/mol. The  $E_a$  values are unstable in the range of  $0.7 < a < 0.99$ , so we draw a conclusion that the dehydration of sample *S1* is a multi-step reaction.

According to linear isoconversional method, the basic data of  $E_a$  collected from the TG curves at various heating rates (5, 10, 15 and 20 °C/min) are obtained. Then, multivariate non-linear regression (Netzsch Thermokinetics) was used to obtain the dehydration mechanism and corresponding kinetic parameters [21]. Considering the dehydration process of *S1*, the initial reversible step was omitted because of the small mass loss. Several models were tested and the initial values of the parameters of  $E_a$  and log *A* were optimized. As shown in Fig. 6, a two-step consecutive reaction model  $A \rightarrow 1B \rightarrow 2C$  was the most-probable one. The first step for dehydration process of hydrogen titanate nanotubes is a reaction of  $n$ th order with autocatalysis with function  $f(a) = (1 - a)^n(1 + K_{cat}a)$ . The second step is a reaction of  $n$ th order with function  $f(a) = (1 - a)^n$ . The kinetic parameters corresponding to this sequence are listed in Table 2.

**Fig. 5** Apparent activation energies and pre-exponential factor of dehydration of S1 with Friedman and FWO method



**Fig. 6** Experimental and fitting TG curves of dehydration of S1 at different heating rates

**Table 2** Kinetic parameters of dehydration of hydrogen titanate nanotube (S1)

Parameter	Value
$\log A1/s^{-1}$	11.0163
$E1$ kJ/mol	85.7662
React. ord. 1	8.2989
$\log K_{cat}$ 1	1.6653
$\log A2/s^{-1}$	5.9175
$E2$ kJ/mol	51.1363
React. ord. 2	2.5122
Foll react. 1	0.5977
Correlation coefficient	0.9995

Owing to the large adsorbed water on titanate nanotubes, a complete description on the  $H_2O$  and hydroxyl groups remains difficult. However, with the help of multivariate non-linear regression calculation, we inferred the dehydration of hydrogen titanate nanotubes preferably performs as a two-step consecutive reaction. The activation energy is 85.7662 kJ/mol for the first stage, and 51.1363 kJ/mol for the second stage. The little reduction of activation energy values is attributed to the increase in the intra and intermolecular vibrations when the temperature increased.

## Conclusions

Thermal analysis technologies were used to investigate chemical formula and dehydration behaviour of hydrogen titanate nanotubes and nanoribbons prepared by  $K_2Ti_2O_5$  with or without water vapour treatment. It was found that their chemical formula is  $TiO_2 \cdot 0.58H_2O$  and  $TiO_2 \cdot 0.6H_2O$ , respectively. And hydrogen titanate nanotubes is probably  $H_2Ti_2O_5$  with some bound water. Moreover, the activation energy of dehydration from hydrogen titanate nanotubes is about 60 kJ/mol according the calculation of Friedman and FWO method. It was shown from multivariate non-linear regression method that dehydration of hydrogen titanate nanotubes is a two-step consecutive reaction. The first step is a reaction of  $n$ th order with autocatalysis. The second step is a reaction of  $n$ th order. The parameters for each step are also given.

**Acknowledgements** The collaborative research between Nanjing University of Technology and University of Hong Kong was assisted by a NSFC-RGC Joint Research Award (No. 20731160614 and HKU 735/07). The authors also thank the support by Changjiang Scholars and Innovative Research Team in University (No. IRT0732), Fund of NSFC (20736002 and 20706028).

## References

- Bavykin DV, Walsh FC. Titanate and titania nanotubes: synthesis properties and applications. Cambridge: Royal Society of Chemistry; 2010.
- Bavykin DV, Friedrich JM, Walsh FC. Protonated titanates and  $TiO_2$  nanostructured materials: synthesis, properties, and applications. *Adv Mater.* 2006;18(21):2807–24.
- Kasuga T, Hiramatsu M, Hoson A, Sekino T, Niihara K. Formation of titanium oxide nanotube. *Langmuir.* 1998;14(12):3160–3.
- Zhang Z, Goodall JBM, Brown S, Karlsson L, Clark RJH, Hutchison JL, et al. Continuous hydrothermal synthesis of extensive 2D sodium titanate ( $Na_2Ti_3O_7$ ) nano-sheets. *Dalton Trans.* 2010;39(3):711–4.
- Kiatkittipong K, Ye C, Scott J, Amal R. Understanding hydrothermal titanate nanoribbon formation. *Cryst Growth Des.* 2010;10(8):3618–25.
- Zhang S, Chen Q, Peng LM. Structure and formation of  $H_2Ti_3O_7$  nanotubes in an alkali environment. *Phys Rev B.* 2005;71(1):014104.

7. Yang J, Jin Z, Wang X, Li W, Zhang J, Zhang S, et al. Study on composition, structure and formation process of nanotube  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ . *Dalton Trans.* 2003;(20):3898.
8. Sun X, Li Y. Synthesis and characterization of ion-exchangeable titanate nanotubes. *Chemistry.* 2003;9(10):2229–38.
9. Lu L, Zhu Y, Li F, Zhuang W, Chan KY, Lu X. Carbon titania mesoporous composite whisker as stable supercapacitor electrode material. *J Mater Chem.* 2010;20(36):7645.
10. Li W, Bai Y, Liu W, Liu C, Yang Z, Feng X, et al. Single-crystalline and reactive facets exposed anatase  $\text{TiO}_2$  nanofibers with enhanced photocatalytic properties. *J Mater Chem.* 2011; 21(18):6718–24.
11. Wei MJ, Zhou J, Lu X, Zhu Y, Liu W, Lu L et al. Diffusion of water molecules confined in slits of rutile  $\text{TiO}_2$  (110) and graphite (001). *Fluid Phase Equilibria.* 2011;302(1–2):316–20.
12. Yang H, Zeng H. Synthetic architectures of  $\text{TiO}_2/\text{H}_2\text{Ti}_5\text{O}_{11}$  center dot  $\text{H}_2\text{O}$ ,  $\text{ZnO}/\text{H}_2\text{Ti}_5\text{O}_{11}$  center dot  $\text{H}_2\text{O}$ ,  $\text{ZnO}/\text{TiO}_2/\text{H}_2\text{Ti}_5\text{O}_{11}$  center dot  $\text{H}_2\text{O}$ , and  $\text{ZnO}/\text{TiO}_2$  nanocomposites. *J Am Chem Soc.* 2005;127(1):270–8.
13. Friedman HL. Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic. *J Polym Sci. Part C.* 1964;6(1):183–95.
14. Ozawa T. A new method of analyzing thermogravimetric data. *Bull Chem Soc Jpn.* 1965;38(11):1881–6.
15. Flynn JH, Wall LA. General treatment of the thermogravimetry of polymers. *J Res Natl Bur Stand.* 1966;70(6):487–523.
16. Majchrzak-Kuceba I. Application of model-free kinetics to the study of dehydration of fly ash-based zeolite. *Thermochim Acta.* 2004;413(1–2):23–9.
17. Zhang K, Hong J, Cao G, Zhan D, Tao Y, Cong C. The kinetics of thermal dehydration of copper(II) acetate monohydrate in air. *Thermochim Acta.* 2005;437(1–2):145–9.
18. Dumitru R, Carp O, Budrugaec P, Niculescu M, Segal E. Non-isothermal decomposition kinetics of  $[\text{CoC}_2\text{O}_4 \cdot 2.5\text{H}_2\text{O}]_n$ . *J Therm Anal Calorim.* 2011;103(2):591–6.
19. Hong J, Guo G, Zhang K. Kinetics and mechanism of non-isothermal dehydration of nickel acetate tetrahydrate in air. *J Anal Appl Pyrol.* 2006;77(2):111–5.
20. Logvinenko V, Fedorov V, Mironov Y, Drebuschak V. Kinetic and thermodynamic stability of cluster compounds under heating. *J Therm Anal Calorim.* 2007;88(3):687–92.
21. Budrugaec P. Application of model-free and multivariate non-linear regression methods for evaluation of the thermo-oxidative endurance of a recent manufactured parchment. *J Therm Anal Calorim.* 2009;97(2):443–51.