

The influence of temperature on the structural behaviour of sodium tri- and hexa-titanates and their protonated forms

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Abstract

The thermal stability of $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$, together with that of their protonated forms was investigated. The influence of temperature on the structural behaviour of tri- and hexa-titanates was studied using DTG, XRD, FTIR and FT-Raman. These results were correlated with the nature of the exchangeable cations using elemental analysis and N_2 -sorption. The tunnel structure of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ revealed a higher thermal stability compared to the layered structure of $\text{Na}_2\text{Ti}_3\text{O}_7$ that shows traces of dimerisation above 800 °C. The sodium forms were observed to be more thermally stable compared to their protonated forms. However, analysis show that ' $\text{H}_2\text{Ti}_6\text{O}_{13}$ ' is much more thermally stable than the layered $\text{H}_2\text{Ti}_3\text{O}_7$ which go through structural changes above 250 °C and suffer a complete structural collapse into anatase/rutile above 800 °C. It was obvious that thermal stability was significantly influenced by the nature of the exchangeable cations and the degree of ion-exchange.

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1. Introduction

Various kinds of titanates have been synthesised which consist of negatively charged layered sheets constructed with corner and edge shared TiO_6 octahedra. Alkali and alkaline earth metal ions (Na, Li, K, etc.) in the interlayers of the titanates, compensate for the negative charge of the TiO_6 sheets [1]. Depending on the alkali or alkaline metal content they assume different structures (layered or cage structures) and they are characterised with different properties. Alkalimetal titanates, $(\text{A}_2\text{Ti}_n\text{O}_{2n+1})$ where $n = 3$ are crystallised into a monoclinic structure that consists of $\text{Ti}_3\text{O}_7^{2-}$ layers held together with exchangeable alkalimetal cations. However, with lower alkalimetal content ($n = 6$), hexa-

titanates are formed, that present a tunnel structure as shown in Fig. 1 [2–4].

Alkali and alkaline metal titanates are potentially important in ion-exchange processes, for ceramic capacitors, as dielectric resonators in microwave oscillators band pass, as a reinforcing agent of plastics, as adiabatic material and as oxygen electrode for potentiometric gas sensors [5–8]. Both alkali metal titanates and hydrogen titanates are *n*-type semiconductors and show excellent photocatalytic activity [1,9–11]. Often titanates are used as precursors for titania-based materials with improved capabilities after an ion-exchange reaction or doping with transition metals [1,12,13].

The influence of temperature on the structural behaviour is of great importance since the structural properties of titanates and their derivatives can have a direct influence on their potential use and practical performance.

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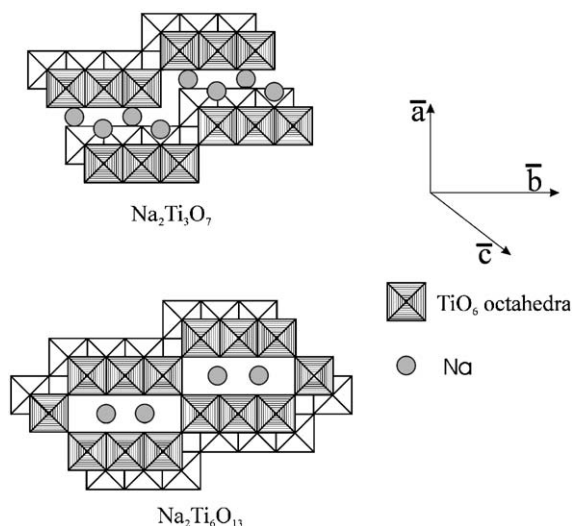


Fig. 1. Schematic representation of layered sodium tri- and hexatitanate structures.

Up to now, very few data are available in literature concerning the influence of temperature on the structural behaviour of tri- and hexa-titanates in their sodium and hydrogen forms. Therefore, a detailed study of thermal stability on these materials was carried out. DTG, XRD, FTIR, and FT-Raman techniques were used to determine thermal stability of $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$. After ion-exchange, the thermal stability of the protonated forms was evaluated using the same techniques.

2. Experimental

2.1. Sample preparation and treatment

$\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$ were synthesised by solid-state reactions from the stoichiometric weights of Na_2CO_3 and TiO_2 (P25, Degussa) (molar ratio 1:6 and 1:3, respectively) followed by an oxidation at 800°C during 20 h. Protonated forms, $\text{H}_2\text{Ti}_3\text{O}_7$ and ' $\text{H}_2\text{Ti}_6\text{O}_{13}$ ' were obtained by acid hydrolyses of their sodium forms. The solid sodium titanates were stirred in a 0.5 mol dm^{-3} HCl solution at 50°C for 3 days. After the ion-exchange process, the samples were dried at room temperature.

Thermal stabilities were tested by calcining the samples in a programmable tube oven to different temperatures while applying a constant air flow.

2.2. Characterisation

Thermal analysis (TGA/DTG) were performed on a Mettler TG 50 thermobalance, equipped with an M3 microbalance and connected to a TC10A processor. DSC measurements were performed in an MOM Q-1500

D instrument. Samples were heated from 30°C up to 900°C at a rate of 5°C min^{-1} . X-ray diffraction (XRD) patterns were collected on a Philips PW 1840 powder diffractometer using Ni-filtered $\text{CuK}\alpha$ -radiation ($\lambda = 1.542\text{ \AA}$). Diffuse Reflectance Infrared Fourier Transform spectra (DRIFT) were measured on a Nicolet 20 DXB FTIR spectrometer, equipped with a Spectra-Tech diffuse reflectance accessory. About 100 scans were taken with a 4 cm^{-1} resolution. During the measurements, the spectrometer was purged with a constant flow of dry air. FT-Raman (Fourier transform Raman) spectra were recorded on a Nicolet Nexus FT-Raman 670 bench with a Ge detector and a 1064 nm Nd:YAG laser. Samples were measured in a 180° reflective sampling configuration. In total, 4000 scans were averaged for each sample with a resolution of 4 cm^{-1} . The laser power was set between 0.4 and 0.7 W. The study of porosity and surface area was performed on a Quantachrome Autosorb 1 MP instrument by recording N_2 -sorption isotherms at 77 K. Specific surface areas were calculated using the BET (Brunauer–Emmett–Teller) model. The deviation in specific surface area data is about 10%. Micropore volumes were calculated from t -plot analysis. The total amount of gas adsorbed at $P/P_0 = 0.95$ was used to determine the total pore volume. The sodium content was determined by elemental analysis carried out on a JEOL JCSA 733 superprobe (electron probe micro-analysis (EPMA)). Interlayer distances were calculated from the XRD diffraction patterns.

3. Results and discussion

The synthesis of $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$, was followed by a thermal analysis (DTG/TGA) (Fig. 2). For both products, similar DTG runs were observed, showing a dehydration peak at 60°C . In addition, 2 peaks were present at 590 and 670°C , reflecting the decomposition of Na_2CO_3 and further weight loss

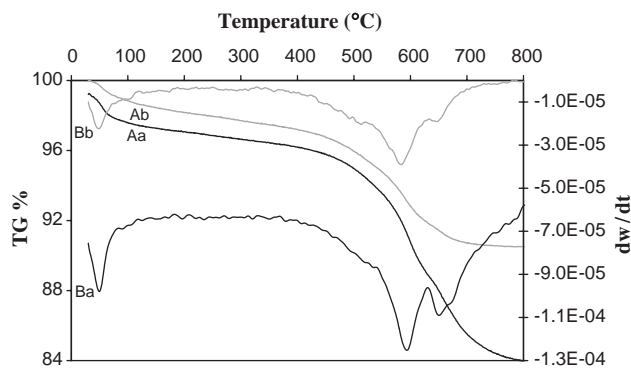


Fig. 2. TGA (A) and DTG (B) curve during synthesis of (a) $\text{Na}_2\text{Ti}_3\text{O}_7$ and (b) $\text{Na}_2\text{Ti}_6\text{O}_{13}$.

during structural rearrangement while forming the layered sodium titanates. During formation, total amount of weight loss was higher for the tri-titanates (16%) compared to the hexa-titanates (9%). This increased weight loss is due to the larger sodium carbonate content ($\text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{O} + \text{CO}_2$) and associated hydration water present in tri-titanates.

After synthesis, XRD patterns of $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$ were comparable with those obtained by Ramirez-Salgado et al. [2] and Peng et al. [14]. XRD diffraction patterns of $\text{Na}_2\text{Ti}_3\text{O}_7$ have the typical peaks for a monoclinic structure and $\text{Na}_2\text{Ti}_6\text{O}_{13}$ has a spectrum characteristic for a base-centred monoclinic structure.

The IR absorption spectra for the Na-tri- and -hexa-titanates are distinctively different from each other and are in agreement with those of Peng et al. [14]. Spectra (Fig. 3B) of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ show two broadbands in the region $700\text{--}1100\text{ cm}^{-1}$ as opposed to a group of four narrower bands for the tri-titanates. No significant spectral changes could be observed after thermal treatment to 800°C in this spectral region, indicating that no important structural transitions take place when heating these sodium-titanates to 800°C (Fig. 3B). Vibrations around $3000\text{--}3200\text{ cm}^{-1}$ and 1500 cm^{-1} assigned to OH-stretching vibrations and H–O–H bending vibrations of hydration water are present before a thermal treatment. However, they will gradually disappear with an increasing thermal treatment due to the dehydration process of the products (Fig. 3A).

The FT-Raman spectra of the Na-tri- and -hexa-titanates show peaks that can be attributed to different Ti–O stretching vibrations in TiO_6 octahedra and distorted TiO_6 octahedra [15] (Fig. 4). Spectra of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ do not change upon heating to higher temperatures. However, after a thermal treatment above 800°C , $\text{Na}_2\text{Ti}_3\text{O}_7$ shows traces of structural transformations into $\text{Na}_2\text{Ti}_6\text{O}_{13}$

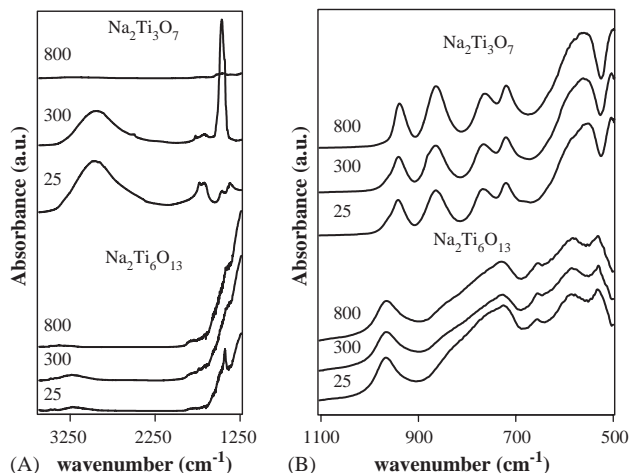


Fig. 3. DRIFT spectra of $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$ pretreated at different temperatures: (A) spectral region between 3300 and 1250 cm^{-1} ; (B) spectral region between 500 and 1100 cm^{-1} .

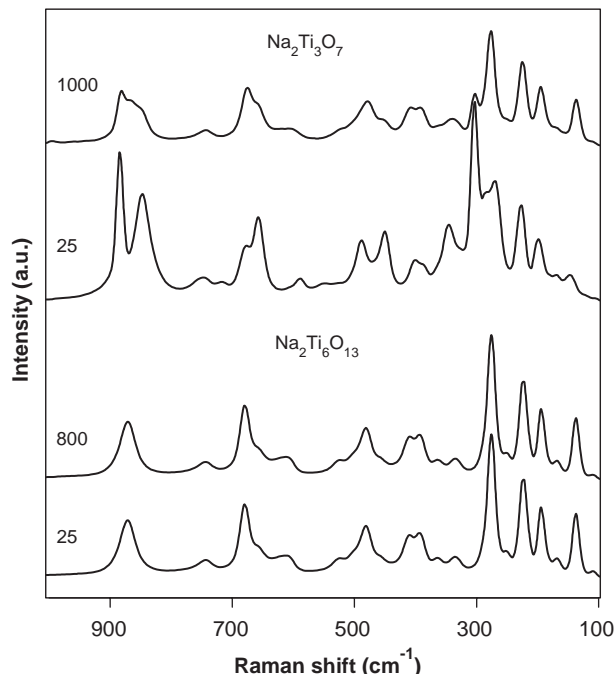


Fig. 4. The FT-Raman spectra of $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$ after a pretreatment at different temperatures.

(dimerisation of $\text{Na}_2\text{Ti}_3\text{O}_7$) and further transformation into anatase/rutile can be assumed.

After a classical acid treatment of their sodium forms, $\text{H}_2\text{Ti}_3\text{O}_7$ and ' $\text{H}_2\text{Ti}_6\text{O}_{13}$ ' were formed due to an ion exchange process. Elemental chemical analysis (EPMA) indicates that in $\text{H}_2\text{Ti}_3\text{O}_7$, 94% of the original Na^+ ions were exchanged by H^+ . However, in the protonated hexa-titanates 99% of the initial Na^+ ions remain in the tunnel structure after ion exchange. These results clearly show that all the Na^+ ions in the layered tri-titanates are accessible for an exchange process with protons and that the Na^+ ions in the hexa-titanates were boxed in by titanate units in the structure, therefore not accessible for ion-exchange. As a result, we can expect that the thermal behaviour of ' $\text{H}_2\text{Ti}_6\text{O}_{13}$ ' will be similar to that of the $\text{Na}_2\text{Ti}_6\text{O}_{13}$ form, except for the presence of exchangeable H^+ at the external surface and in a few open channels. (The acid treated $\text{Na}_2\text{Ti}_6\text{O}_{13}$ will be denoted as ' $\text{H}_2\text{Ti}_6\text{O}_{13}$ ' in order to indicate the ion-exchange treatment even though only a very small amount of Na^+ has been replaced by H^+ .)

Compared to the sodium forms, $\text{H}_2\text{Ti}_3\text{O}_7$ and ' $\text{H}_2\text{Ti}_6\text{O}_{13}$ ' show a significantly different behaviour with respect to their thermal stability. As shown in the DTG (Fig. 5) of $\text{H}_2\text{Ti}_3\text{O}_7$ a dehydration peak at 60°C and at 250°C could be observed. The peaks at 590 and 670°C are absent due to previous heating as the samples were prepared. The peak at 250°C is due to the condensation of OH groups to give H_2O during a structural

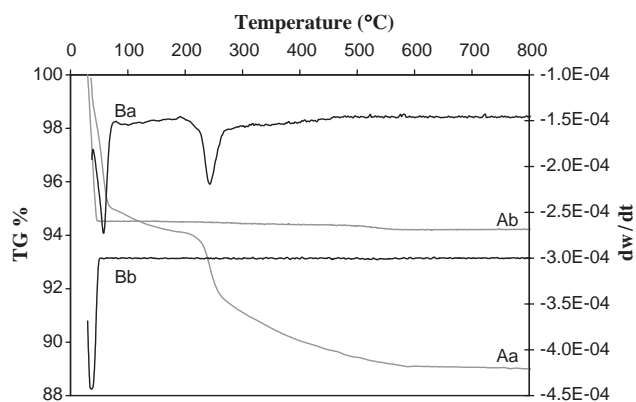


Fig. 5. TGA (A) and DTG (B) curve after synthesis and acid hydrolyses of (a) $\text{Na}_2\text{Ti}_3\text{O}_7$ and (b) $\text{Na}_2\text{Ti}_6\text{O}_{13}$.

transformation. This was confirmed by an exothermic peak at 250°C in DSC. However, in DTG measurement of ' $\text{H}_2\text{Ti}_6\text{O}_{13}$ ', only the dehydration peak at 60°C can be detected. The absence of weight loss at 250°C for ' $\text{H}_2\text{Ti}_6\text{O}_{13}$ ', suggests a higher thermal stability compared to the tri-titanate product. This observation could be confirmed by XRD, FTIR, and FT-Raman data and the nature of the structural transformation could be identified. The XRD patterns (Fig. 6), obtained after heating the $\text{H}_2\text{Ti}_3\text{O}_7$ and ' $\text{H}_2\text{Ti}_6\text{O}_{13}$ ' samples, clearly show a condensation and structural transformation of $\text{Ti}_3\text{O}_7^{2-}$ into anatase ($250^\circ\text{C} < T < 700^\circ\text{C}$) and finally rutile after heating temperatures above 700°C . These structural changes were not observed for ' $\text{H}_2\text{Ti}_6\text{O}_{13}$ ' due to stabilising effect of the high amount of Na^+ ions that remained in the structure after ion-exchange. The stabilising effect of Na^+ ions in the structure can be explained by the absence of H^+ ions, which facilitate the acid catalysed condensation of OH groups during structural transformation. Comparable observations were found in the FTIR spectra of protonated trititanates and protonated sodium hexa-titanates (Fig. 7). Significant differences in the spectra of $\text{H}_2\text{Ti}_3\text{O}_7$ in the range of 250 – 700°C and above 700°C could be observed. The different bands assigned to various Ti–O–Ti stretching vibrations in $\text{H}_2\text{Ti}_3\text{O}_7$ observed at room temperature have gradually decreased above 250°C . At the same time a broadband between 500 and 750 cm^{-1} characteristic for anatase/rutile appears. These results suggest a collapse of the layered $\text{Ti}_3\text{O}_7^{2-}$ structure and a structural transformation into anatase ($250^\circ\text{C} < T < 700^\circ\text{C}$) and rutile ($T > 700^\circ\text{C}$) due to condensation of OH groups with the loss of water. Similar to the results obtained from XRD and DTG, these thermal effects were not detected in IR spectra of ' $\text{H}_2\text{Ti}_6\text{O}_{13}$ '. However, the disappearance of OH stretching vibrations (isolated and bridged OH-groups) in the 2800 – 3200 cm^{-1} region with increasing temperatures,

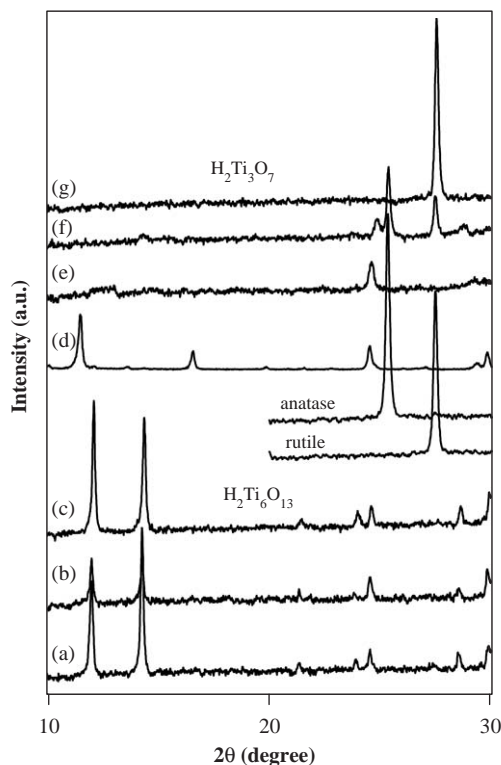


Fig. 6. XRD spectra of ' $\text{H}_2\text{Ti}_6\text{O}_{13}$ ' at (a) 25°C , (b) 300°C , (c) 800°C , $\text{H}_2\text{Ti}_3\text{O}_7$ at (d) 25°C , (e) 300°C , (f) 800°C , (g) 1000°C together with the rutile and anatase spectra.

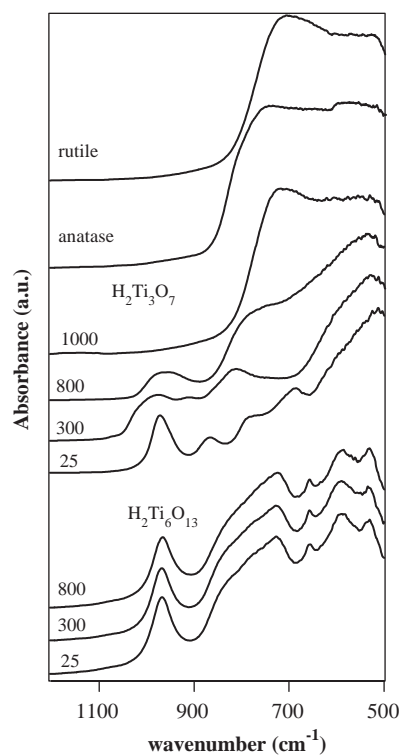


Fig. 7. DRIFT spectra of $\text{H}_2\text{Ti}_3\text{O}_7$ and ' $\text{H}_2\text{Ti}_6\text{O}_{13}$ ', heated to different temperatures together with the DRIFT spectra of anatase and rutile.

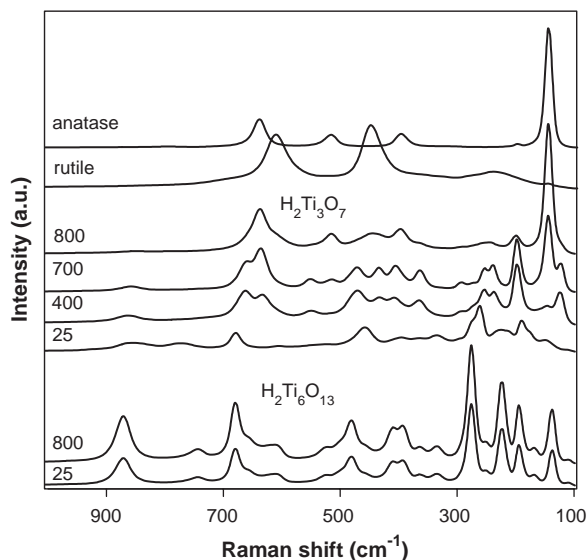


Fig. 8. FT-Raman spectra of $\text{H}_2\text{Ti}_3\text{O}_7$ and ' $\text{H}_2\text{Ti}_6\text{O}_{13}$ ' pretreated at different temperatures.

was equal for both protonated tri-titanates and protonated sodium hexa-titanates. Additionally, the indication of structural changes in the protonated tri-titanate compounds can be illustrated by FT-Raman spectroscopy (Fig. 8). Above 250°C bands of anatase (150 , 395 , 517 and 638 cm^{-1}) and later a second phase ($>700^\circ\text{C}$) of rutile (446 and 611 cm^{-1}) become more and more pronounced. As observed in XRD, DTG and IR, above 250°C , traces of an anatase/rutile-like phase starts to form, which develops into a mixed anatase/rutile phase above 700°C . These phase transformations could not be detected in the protonated sodium hexa-titanate with FT-Raman as was previously stated.

The remarkably higher thermal stability of ' $\text{H}_2\text{Ti}_6\text{O}_{13}$ ' compared to $\text{H}_2\text{Ti}_3\text{O}_7$, and the results from the elemental analysis (EPMA) suggest that the increased stability of ' $\text{H}_2\text{Ti}_6\text{O}_{13}$ ' is due to the amount of residual Na^+ ions in the structure of ' $\text{H}_2\text{Ti}_6\text{O}_{13}$ ' after ion-exchange. Therefore, the collapse of the tri-titanate layers can be ascribed to the absence of stabilising Na^+ ions within the layered structure. The incomplete ion-exchange of protonated sodium hexa-titanates could be assigned to the accessibility of the interlayer space for ion exchange processes. An additional indication to illustrate the difference in accessibility could be derived from the differences in surface area (derived from N_2 adsorption/desorption at -196°C) between the Na^+ and protonated forms at room temperature. $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{H}_2\text{Ti}_3\text{O}_7$ have specific surface areas of $2.5\text{ m}^2\text{ g}^{-1}$ and $6.5\text{ m}^2\text{ g}^{-1}$, respectively. Moreover, the interlayer distances were calculated as 0.83 nm and 0.78 nm , respectively. Owing to the smaller size of the H^+ ions, the N_2 adsorption can occur on both external surface and between the layers, therefore higher surface

areas are observed after ion-exchange. However, no differences in surface area between $\text{Na}_2\text{Ti}_6\text{O}_{13}$ and ' $\text{H}_2\text{Ti}_6\text{O}_{13}$ ' could be detected ($2.8\text{ m}^2\text{ g}^{-1}$) that for both only reflect the external surface area of the crystal particles. Calculation of the interlayer distances of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ and ' $\text{H}_2\text{Ti}_6\text{O}_{13}$ ' (for both 0.74 nm) confirms this conclusion.

4. Conclusions

In conclusion, the results reported here clearly reveal that the tri-titanate layered structures are thermally less stable compared to the hexa-titanate tunnel structures. Furthermore, the stabilising effect of the Na^+ ions in the structure causes a higher structural stability compared to the protonated forms, especially in the tri-titanates. Moreover, heating to temperatures higher than 250°C gives rise to a lower hydrophilic surface behaviour in the protonated tri- and hexa-titanates. Only at higher temperatures ($T > 700^\circ\text{C}$) traces of a structural conversion of $\text{Na}_2\text{Ti}_3\text{O}_7$ into hexa-titanates or anatase/rutile could be detected. For the protonated titanates, significant structural changes were observed for the $\text{H}_2\text{Ti}_3\text{O}_7$. After heating to temperatures between 250 and 700°C , a collapse of the layered structure was evident and for temperatures above 700°C a phase transformation into anatase and rutile was detected. Because of the stable tunnel structure and the larger amount of residual Na^+ ions in ' $\text{H}_2\text{Ti}_6\text{O}_{13}$ ' only structural transformations were possible above 1000°C .

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