Effects of thermal treatment of nanostructured trititanates on their crystallographic and textural properties

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Abstract

Nanostructured titanates (TTNT) with general formula Na\textsubscript{x}H\textsubscript{2}/C0\textsubscript{x}Ti\textsubscript{3}O\textsubscript{7}/C1\textsubscript{n}H\textsubscript{2}O were synthesized by hydrothermally reacting different TiO\textsubscript{2} anatase (distinct crystal sizes) with NaOH at 120 °C followed by washing with water or diluted acid and drying of the precipitate. The resulting powders with different sodium contents were submitted to various calcination temperatures up to 800 °C and each calcined product was characterized as for its phase structure, composition, crystallite size and textural properties, namely BET surface area, mesopore volume and pore size distribution. Thermal transformations of TTNT samples were investigated by monitoring the modifications on crystallographic (X-ray diffraction) and textural (N\textsubscript{2} desorption isotherms) properties, revealing the influence of the type of starting anatase and sodium content over the stability of TTNT. Moreover, a detailed study on the reduction of the interlayer distance in TTNT samples upon thermal treatment allowed corroborating the formation of an intermediate nanostructured hexatitanate, just before phase transformation into the corresponding TiO\textsubscript{2} polymorphs and/or titanate crystals, depending on the sodium content and calcination temperature.

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1. Introduction

In the latest years, there has been an increasing interest on nanostructured TiO\textsubscript{2} materials owing to their enhanced surface area and potential applications in catalysis [1–3] and photocatalysis [4–6]. In particular, TiO\textsubscript{2}-derived nanotubes obtained by a hydrothermal alkali treatment have attracted special attention since the innovative work of Kasuga et al. [7,8], who first synthesized long and uniform nanotubes with external diameter as small as 10 nm by simply treating crystalline TiO\textsubscript{2} in highly concentrated NaOH aqueous solution at relatively low temperatures...
(100–150 °C). Many groups have tried to modify the process and to elucidate the mechanism of formation as well as the true composition and crystalline structure of the resulting TiTania or TiTanate NanoTubes (TTNT).

Apparently, upon this synthesis path there is a common agreement that after breaking chemical bonds of the starting tridimensional TiO2 structure, planar entities are formed and converted through a sheet folding or wrapping mechanism into nanotubes with multi-layered walls. Different crystal structures and compositions have been proposed to describe the TTNT structure, such as TiO2 anatase [7,9–13], bititanate Na_xH_2/C0_xTi_2O_4(OH)_2 [14], trititanates H_2Ti_3O_7 [15–19], H_2Ti_3O_7·nH_2O [20], Na_xH_2–xTi_3O_7 [21,22], tetratitanate H_2Ti_4O_9·H_2O [23,24] and lepidocrocite-like titanate H_(Ti_2–x/3Ti_x/3)O_4 [25,26]. In two recent papers [27,28] we have demonstrated that TTNT actually possess trititanate structure with general formula Na_xH_2/C0_xTi_3O_7/C1_nH_2O, where x and n depend on the degree of sodium-proton exchange during washing procedure; bound water is intercalated between wall layers and its amount (n) is directly proportional to the sodium content (x).

The investigation on thermal stability of TTNT is of paramount importance for the practical use of nanotubes and in designing calcined-derived materials with appropriate chemical and textural properties. Indeed, many authors have been studying thermal transformation of TTNT samples to unveil its original crystal structure and characterize the products upon heat treatment at different temperatures [6,16,20–22,27,29–32], sometimes aiming to control the microstructure of TiO2-derived nanotubes. Different phase structures have been reported for the calcined nanotubes, what may be ascribed to the distinct synthesis and post-treatment conditions applied in each work and sometimes due to wrong interpretation. Hardly any research has been dedicated to evaluate the influence of synthesis parameters on the behavior of the resulting TTNT after heat treatment, unless very few exceptions [29]. Moreover, few papers have provided a complete characterization of the calcined samples uniting crystal structure and textural properties.

In the present study, nanostructured titanates were prepared via hydrothermal alkali treatment (Kasuga et al.’s method) starting from two anatase sources with different average crystal sizes. Each reaction product was washed distinctly to provide three levels of sodium content. Subsequently, these six TTNT samples were submitted to various calcination temperatures up to 800 °C and each calcined product characterized as for its phase structure and composition, crystallite size and pore size distribution. Having in mind its potential applications, it was intended to provide information on the thermal stability of TTNT and on the crystal and pore structure of its calcined-derived materials, as a function of the starting anatase particle size and remanent sodium content in TTNT.

2. Experimental

2.1. TiO2 anatase raw materials

Two distinct commercial TiO2 anatase powders were used in this study: A1 (Tiona® AT1, supplied by Millenium) and A2 (FINNTi®-S140, supplied by Kemira). Their average crystal size were estimated from their XRD patterns based on Scherrer equation as, respectively, 220 and 8 nm, in good agreement with their morphologies examined by TEM. BET surface areas of 7 and 150 m²/g were, respectively, measured via N₂ adsorption at −196 °C, after degassing samples A1 and A2 at 300 °C.

2.2. Synthesis of TTNT

Anatase powders A1 and A2 (~3 g on TiO2 basis) were separately added to 50 mL of NaOH 10 M sol. and charged to stainless steel Parr reactor (model A-500) equipped with electrical heating, temperature control and magnetic stirrer. The reactors were sealed, heated to 120 °C and the mixtures left at this temperature for 30 h with A1 and 15 h with A2. The reaction time was established as minimum to ensure complete conversion of the starting TiO₂ into a titanate structure according to XRD monitoring. Syntheses were carried out in replicates in order to collect enough material for this work. As-synthesized precipitate in each case was submitted to three different washing procedures: (i) with deionized water until filtrate with pH ~ 7–8; (ii) reslurring with HCl solution at pH 4.5 alternated with water washing; (iii) reslurring with HCl solution at pH 1.5 alternated with water washing. The wet filter-cakes were dried at 120 °C overnight in an air-circulating oven generating the corresponding TTNT/A1 and TTNT/A2 samples listed in Table 1 with sodium content at three different levels: <0.5% Na (L = low); 4–6% Na (M = medium); ~10% Na (H = high). The samples were divided into equal portions for calcination at temperatures varying from 200 to 800 °C for 2 h in a muffle.
2.3. Characterization tools

Sodium content was measured on as-such (dried) basis by flame photometry after dissolving TTNT in concentrated H₂SO₄. X-ray diffraction (XRD) analyses were performed on a powder diffractometer (Rigaku XRD-6000), operating with Cu Kα radiation at 40 kV and 35 mA, scan speed of 0.24° min⁻¹, step size of 0.02° and preset time of 5s. In some XRD patterns Rietveld refinement was performed with the software Topas 6.2 supplied by Bruker. Some samples were analyzed by high-temperature X-ray diffraction (HT-XRD) with in situ calcination from 100 to 500 °C and scanning within a narrow low-angle 2θ range, using a Bruker D-5000 diffractometer equipped with a PSD detector and Cu Kα radiation operated at 40 kV and 35 mA. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) were recorded using a Gatan CCD camera on a JEOL-2010 microscope operating at 200 kV. Specimens for TEM observation were prepared by dispersing the powder in alcohol by ultrasonic treatment, then dropping onto a holey carbon film supported by a copper grid. Thermogravimetry was performed in a Shimadzu TGA51-H instrument under dry air flow (50 mL/min); temperature range was 25–800 °C with a heating-up rate of 5 °C/min. Differential thermal analyses was conducted in a Shimadzu DTA-50 instrument at three different heating-up rates of 5, 10 and 20 °C/min. Textural properties of the powder samples, pretreated at 120 °C under vacuum down to 50 mTorr, were characterized by N₂ adsorption at 196 °C on a Micromeritics TriStar 3000 V6.03 instrument. Specific surface area was calculated by using the classic BET equation in the P/P₀ range of 0.06–0.21; pore volume and pore size distribution within 2–60 nm diameter range was determined by means of the Barrett–Joyner–Halenda (BJH) algorithm method using the desorption branch of the isotherm. Average pore diameter was calculated from the desorption isotherm as 4V/A, where V is the specific pore volume and A is the specific surface area.

3. Results and discussion

3.1. Characterization of the as-synthesized TTNT samples

SEM images revealed that the starting anatase granules, whatever its size, were completely transformed into large particles of aggregated fibers [28]. This general morphology did not change after proton exchange. As shown in Fig. 1, the complete conversion of anatase was confirmed by XRD analysis, which also evidenced the formation of layered titanate patterns with relative intensities and position of the first peak (interlayer distance) dependent on the degree of proton exchange. The relative ratio between peaks at 24° and 28° 2θ is a useful fingerprint to infer about the degree of hydrogen exchange in TTNT. Our synthesized titanates could be assigned to sodium trititanate (PDF 31-1329, space group: P2₁/m (No. 11)) and/or hydrogen trititanate (PDF 47-0561, space group: C2/m (No. 12)) depending on the degree of sodium exchanged. Assuming the general formula NaₓH₂₋ₓTi₃O₇₋ₓnH₂O for the obtained titanates [27,28], measured sodium content combined with thermogravimetric analysis allowed calculating the approximate composition of each sample as displayed in Table 1. It was evident that the amount of chemically bound water, intercalated between layers, was proportional to the existing sodium in this layered structure [28].

When observed by TEM (Fig. 2), all products showed formation of multi-walled nanotubes, either randomly oriented or as aligned bunches, coexisting more or less with layered sheets or incompletely rolled-up tubes. Nanotubes synthesized from anatase A1 were very similar in their dimensions with external (internal) diameters ranging from 6 to 10 (3–5) nm, walls of three to five layers and length of several hundreds of nanometers. In contrast, TTNT samples obtained from A2 visually showed lower yields of well-defined nanotubes, which, when found, were systematically and significantly larger than those found in TTNT-A1 samples, with external (internal) diameters ranging from 10 to...
(4–10) nm and thicker walls containing higher number of layers. In any case, plenty of multi-walled nanoparticles could be found with an average interlayer distance measured by TEM and confirmed by SAED (insets in Fig. 2a and b) of 0.74–0.75 nm, which is significantly smaller than the interlayer distance measured based on the position of the first peak in XRD pattern (see Table 1).

3.2. Characterization of the calcined-derived samples

3.2.1. XRD studies

XRD patterns of the calcined samples are displayed in Fig. 3. In those cases where sufficiently crystalline phases were present, Rietveld method was applied and phase composition could be quantitatively determined; the fitness of the simulated XRD patterns to the experimental patterns was good and the results are summarized in Table 2. Confirming our previous results [27], it became evident that thermal transformation of TTNT was primarily a function of the sodium content leading to the following paths regarding XRD detectable phases:

Low sodium:

\[ \text{TTNT} \rightarrow \text{TiO}_2(B) + \text{anatase} \rightarrow \text{anatase} + \text{rutile} \]

Medium sodium:

\[ \text{TTNT} \rightarrow \text{TiO}_2(B) + \text{Na}_2\text{Ti}_6\text{O}_{13} \rightarrow \text{anatase} + \text{Na}_2\text{Ti}_6\text{O}_{13} + \text{rutile} \]

High sodium:

\[ \text{TTNT} \rightarrow \text{Na}_2\text{Ti}_6\text{O}_{13} + \text{Na}_2\text{Ti}_3\text{O}_7 \]

The use of anatase with distinct crystal size as raw material for the TTNT synthesis did not change this general scheme and seems to corroborate the findings of our recent study in that TTNT structure and its dependence on sodium...
content were not affected by the crystallite size of the starting anatase [28]. However, it was possible to verify some differences on the rate of thermal transformations of TTNT as a function of the anatase raw material. At high sodium content, the onset of very fine peaks of sodium trititanate and hexatitanate occurred at 600 °C for sample TTNT-A2/H whereas such peaks were hardly visible for sample TTNT-A1/H at this temperature (Fig. 3c versus Fig. 3f). At medium sodium content, one could see that the onset of anatase phase occurred at 500 °C for sample TTNT-A2/M and at 600 °C for TTNT-A1/M (Fig. 3b versus Fig. 3e). As it can be seen from quantitative data in Table 2 at sodium content nearly zero, transformation from TiO₂(B) into anatase and from this into rutile occurred more readily with sample TTNT-A2/L. Actually, rutile could not be found after calcining sample TTNT-A1/L up to 800 °C. These results at rather constant sodium suggest that slightly less stable nanostructured titanates are obtained from anatase with smaller crystals, leading to faster thermal transformations of TTNT-A2 samples, according to the sodium content.

By examining Fig. 3, one can conclude that sodium in TTNT helps preserving the trititanate structure upon heat treatment. Samples TTNT-A1/L and TTNT-A2/L with very low sodium content and composition nearly the fully hydrogenated trititanate, H₂Ti₃O₇, converted into metastable TiO₂(B) and anatase at relatively lower temperatures (400 °C). Indeed, the appearance of the TiO₂(B) as an intermediate phase is expected for the thermal decomposition of hydrogen exchanged titanates with formula H₂TiₙO₂ₙ₊₁ (3 ≤ n ≤ 6) [33]. Due to its wide and low intensity reflections with some coinciding with anatase positions, TiO₂(B) may be overlooked in XRD analysis by those dealing with thermal transformation of nanostructured titanates. According to our data (Fig. 3 and Table 2), TiO₂(B) was generated from TTNT samples with sufficiently hydrogen in the trititanate composition and survived between about 350 and
550 °C. This life range is in fairly agreement with the study of Armstrong et al. [32]. It is highly improbable the existence of TiO$_2$(B) after calcining TTNT at 700–800 °C as Suzuki and Yoshikawa thought to have demonstrated [20].

On the samples with low and medium sodium content, where anatase appeared as a product of TTNT calcination, the double-Voight method [34] also allowed calculating the average crystallite size of this phase. From the results shown in Table 3, some observations could be made: (i) the growth of the anatase crystallites with calcination temperature and their much larger size when coexisting with rutile, in reasonable agreement with the results recently

Table 2
Summary of the Rietveld analysis of the multiphase materials obtained after heat treatment of TTNT samples

<table>
<thead>
<tr>
<th>Percentage of Na in TTNT</th>
<th>Temperature (°C)</th>
<th>From A1</th>
<th>From A2</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.5</td>
<td>800</td>
<td>66.3% Na$_2$Ti$<em>6$O$</em>{13}$; 33.7% Na$_2$Ti$_4$O$_7$</td>
<td>58.0% Na$_2$Ti$<em>6$O$</em>{13}$; 42.0% Na$_2$Ti$_3$O$_7$</td>
</tr>
<tr>
<td>4.8–6.4</td>
<td>800</td>
<td>84.3% Na$_2$Ti$<em>6$O$</em>{13}$; 12.3% TiO$_2$ rutile; 3.4% TiO$_2$ anatase</td>
<td>83.6% Na$_2$Ti$<em>6$O$</em>{13}$; 10.3% TiO$_2$ rutile; 6.0% TiO$_2$ anatase</td>
</tr>
<tr>
<td>0.2–0.3</td>
<td>400</td>
<td>51.8% TiO$_2$(B); 48.2% TiO$_2$ anatase</td>
<td>48.6% TiO$_2$(B); 51.4% TiO$_2$ anatase</td>
</tr>
<tr>
<td>0.2–0.3</td>
<td>550</td>
<td>10.0% TiO$_2$(B); 90.0% TiO$_2$ anatase</td>
<td>3.2% TiO$_2$(B); 96.8% TiO$_2$ anatase</td>
</tr>
<tr>
<td>0.2–0.3</td>
<td>800</td>
<td>100% TiO$_2$ anatase</td>
<td>3.5% TiO$_2$ rutile; 96.5% TiO$_2$ anatase</td>
</tr>
</tbody>
</table>
reported by Yu et al. [6]; (ii) the similar crystal size values of anatase derived from TTNT samples synthesized from anatases with completely different crystal sizes (220 nm versus 8 nm).

The first diffraction peak of TTNT patterns corresponds to the interlayer distance of the multi-walled nanostructured titanates. The reason why the $d$-values of our as-synthesized TTNTs measured from XRD patterns was within a higher range (0.82–0.91 nm) than that of bulk trititanates ($d$-values of (2 0 0) plane for H$_2$Ti$_3$O$_7$ and (1 0 0) for Na$_2$Ti$_3$O$_7$ are 0.78 and 0.84 nm, respectively) has been previously explained [27,28] by the swelling effect caused by the presence of water molecules between the corrugated layers of Na$_{2-x}$H$_x$Ti$_3$O$_7$, increasing the interlayer distance. Another evidence of this assumption has been found with the shift of the first diffraction peak towards higher 2$\theta$ value after calcination (dehydration) of TTNT samples [20,27,31]. In the present work, we have found that such shrinkage of the interlayer space occurred in a similar way for TTNT samples derived from anatase precursors with different sizes. As shown in Fig. 4a, the increase in calcination temperature led to a significant reduction of the interlayer distance before the layered structure was collapsed. The samples with higher sodium contents prolonged the life of the layered structure and due to their higher content of interlayer water also showed the largest drop of interlayer distance. However, this drop occurred only after 300°C when most of dehydration of the TTNT structure was supposedly to have taken place according to TGA/DTA data. The reason for this behavior was accounted to the easy rehydration of the calcined TTNT samples – as verified by auxiliary thermogravimetric experiments – thus allowing to recover the interlayer expansion after reinsertion of H$_2$O from atmosphere. To resolve this question, samples TTNT-A1/H and TTNT-A2/H containing the highest amount of intercalated water (Table 1) were submitted to in situ XRD measurements between 100 and 500°C (HT-XRD) aiming at specific analysis of the first peak region. As shown in Fig. 4b, most of the significant shift occurs upon calcination at 200°C. This is in accordance with the DTA results of such samples, which indicate that intercalated water leaves TTNT structure mostly between 130 and 180°C (see second endothermic peaks arrowed in Fig. 5b), whereas no other endothermic peak besides that of physisorbed water (<100°C) could be found for their counterparts with low sodium (Fig. 5a). An important observation derived from both ex situ and in situ XRD results (Fig. 4a and b) is that interlayer distance just before collapsing of the layered structure tended to stabilize at a value within 0.74–0.77 nm, which is below the theoretical range of 0.787–0.837 nm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size of anatase (nm) (estimated error)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400°C</td>
</tr>
<tr>
<td>TTNT-A1/M</td>
<td>–</td>
</tr>
<tr>
<td>TTNT-A1/L</td>
<td>4.8 (0.5)</td>
</tr>
<tr>
<td>TTNT-A2/M</td>
<td>–</td>
</tr>
<tr>
<td>TTNT-A2/L</td>
<td>5.4 (0.3)</td>
</tr>
</tbody>
</table>

![Fig. 4. (a) Interlayer distance measured by XRD of calcined TTNT samples before collapsing the layered structure. (b) Interlayer distance measured by HT-XRD with in situ calcination of samples TTNT-A1/H and TTNT-A2/H.](image-url)
assuming the dehydrated trititanate composition: Na$_{3}$H$_{2-x}$Ti$_{3}$O$_{7}$. That means the reduction of interlayer distance on calcined TTNT before collapse could not be only explained by the release of intercalated water. This range of 0.74–0.77 nm, is closer to the value of 0.74 nm assigned to the (2 0 0) $d$-spacing for Na$_{2}$Ti$_{6}$O$_{13}$. Therefore, we suggest that after dehydration and before TTNT is collapsed, the trititanate is at least partially converted into hexatitanate nanotubes through a well known displacive transformation [35] where Ti$_{3}$O$_{7}^{2-}$ units of adjacent layers are connected keeping the compensating cation trapped in a tunnel like structure, typical of the hexatitanate. It is worth reminding that interlayer distance in TEM/SAED experiments was also reluctantly measured as nearly 0.74–0.75 nm (Fig. 2). As earlier suggested [27], this is also explained by the transformation of trititanates into their corresponding hexatitanates nanotubes inside TEM chamber as a consequence of the intrinsic reducing atmosphere (vacuum of 10$^{-8}$ Torr) and the heating caused by the electron beam.

At higher temperatures, depending on the sodium content, this intermediate nanostructured hexatitanate would then be transformed reconstructively into TiO$_{2}$(B) [33] or grown up to much larger crystals of sodium hexatitanate. At very high sodium content, the trititanate nanostructure should be more resistant against phase transformation, so that complete transformation to hexatitanate would be so retarded that some unconverted Na$_{2}$Ti$_{3}$O$_{7}$ nanoparticles remaining after complete dehydration of TTNT would evolve directly to larger crystals of sodium trititanate at higher temperatures in competition with its transformation into hexatitanate.

Another contribution of the present paper is about the onset temperature for anatase-to-rutile phase transformation when calcining TTNT samples. This is mainly regarded to the TTNT samples with lower sodium contents since this element stabilizes the titanate structure leading to highly crystalline sodium titanates as dominating phases prevailing over TiO$_{2}$ phases. Different onsets on anatase-to-rutile phase transformations derived from TTNT are reported in literature. Tsai and Teng [29] demonstrated that this onset was shifted to higher temperatures when TTNT was synthesized at higher hydrothermal temperatures; their TTNTs produced at 110, 120 and 130 °C led to onsets, respectively, occurring at 400, 700 and 900 °C. This could not explain the results found by Yu et al. [6] and Ferreira et al. [31], who prepared their nanotubes at reaction temperatures of 150 and 170 °C and observed the corresponding onset temperatures within 600–800 °C. According to Tsai and Teng’s prediction, our TTNT samples synthesized at 120 °C would result in an onset around 700 °C. Indeed, it was nearly the case for heat-treated TTNT-A2/L derived from starting anatase A2 with smaller crystallite, but not for TTNT-A1. No surprise, those authors used as raw material a commercial TiO$_{2}$ with particle size of $\sim$21 nm, which is closer to that of A2 than that of A1. A logical conclusion is that the rate of thermal transformation in TTNT is not only dependent on the synthesis temperature, but also on the particle size of the starting anatase.

![Fig. 5. DTA curves at three different heating rates of samples: (a) TTNT-A2/L and (b) TTNT-A2/H.](image-url)
3.2.2. Nitrogen adsorption studies—textural properties

The \( \text{N}_2 \) adsorption–desorption isotherms measured for the studied TTNT samples exhibited hysteresis loops typical of mesoporous solids. However, the shape of hysteresis loop in TTNT was dependent both on the sodium content and mainly on the type of precursor anatase, as previously reported and discussed [28]. The purpose of the present paper is to study the textural changes of the TTNT samples after progressive thermal treatment. As illustrated in Fig. 6 for TTNT samples with medium sodium content, the isotherm profile remained practically unaltered from 120 to 400 °C with TTNT derived from A1 (Fig. 6a), while some change could be observed at 400 °C with TTNT derived from A2 (Fig. 6b). This relatively earlier change in textural properties upon progressive calcination seems to confirm the faster thermal transformation of the TTNT-A2 samples as anticipated by XRD analysis. Such relative behavior in hysteresis loops as a function of calcination temperature was also found for the series with low and high sodium content. On the other hand, the hysteresis profile noticed in TTNT-A2 samples calcined up to 400 °C, predominantly of type H3 according to IUPAC classification [36], evolved when calcined at higher temperatures (see isotherms at 600 °C in Fig. 6a versus Fig. 6b) to the same profile as that of TTNT-A1, which is a mix of H1 and H3 types. Such mesoporous material was tentatively assigned to interparticle spaces due to, respectively, well-defined crystallites giving rise to uniform pores and due to non-rigid aggregates giving rise to slit-shaped pores. Isotherms in Fig. 6 also evidenced smaller \( \text{N}_2 \) adsorption loads per gram of solid with increasing calcination temperature.

The drop in BET surface area with calcination temperature, as shown in Fig. 7, is in accordance with previous observations [6,22,27,29], but in this paper such behavior was investigated with TTNT materials synthesized from distinct starting titania. In all cases, surface area reduced steadily as long as nanotubes survived and decreased sharply upon further thermal treatment, indicating sintering of the tubes and destruction of the titanate lamellar structure. This transition occurred earlier for the samples with the least sodium content, corroborating the stabilization effect of TTNT structure promoted by sodium. Although less evident from the change in curve slopes of the plot in Fig. 7, it was also possible to suggest an earlier thermal collapse for those TTNTs derived from anatase A2 in comparison with their counterparts derived from A1, hence in agreement with the XRD results described in previous section. Above 500 °C, surface areas tended to converge to the same level despite their different phase compositions (Table 2 and Fig. 3).

The pore size distributions of the calcined samples are shown in Fig. 8. Pore volume in \( y \)-axis is normalized per logarithm of pore diameter, which conventionally better represents the frequency distribution. The reliability of the pore volume distribution using BJH algorithm is restricted to the mesopores range displayed between 2 and 60 nm. The profile of pore size distribution (PoSD) was remarkably dependent on the crystal size of the precursor anatase.

On TTNT-A1 samples a bimodal distribution could be distinguished, i.e., a small peak centered between 2 and 5 nm and another one with a wide distribution ranging from 5 to 60 nm (Fig. 8a–c). The former is supposed to correspond to the inner space of the nanotubes while the broader mode covering the largest mesopore range accounts for the interspace generated from the aggregation of nanotubes. These assumptions are in very good agreement with low

![Fig. 6. \( \text{N}_2 \) adsorption–desorption isotherms of: (a) TTNT-A1/M samples and (b) TTNT-A2/M samples, calcined at different temperatures.](image)
magnification TEM images showing TTNT aggregates and high magnification ones revealing most individual nanotubes with inner diameters between 3 and 4 nm. Up to 300 °C TTNT texture was apparently preserved since PoSD has not been significantly altered irrespective of sodium content. After calcination at 400–500 °C, the pore volume within 2–5 nm was remarkably reduced whereas the second mode within 5–60 nm was not significantly affected, thus indicating that the tubular morphology (hollowed) is progressively collapsed into their corresponding nanorods without much change of the external morphology, which explains the preservation of the interparticle size distribution. However, above 500 °C, not only contribution of pores within 2–5 nm was vanished indicating complete absence of nanotubes, but also the large peak within 5–60 nm started shifting to a large pore diameter range, indicating growth of the nanoparticles.

Another distinct picture regarding PoSD has been found for the TTNTs obtained from anatase A2 of lower crystal size (Fig. 8d–f). A wide distribution covering all mesopore size range was observed without clear evidence of bimodal distribution. This fact did not allow an easy discrimination between mesopores attributed to inner space of nanotubes and those attributed to interparticle space. Attention should be paid to the PoSD of sample TTNT-A2/H (Fig. 8f), where a false narrow peak is observed at 3.7 nm due to an artifact caused by a spontaneous evaporation of the capillary condensed liquid owing to the so called tensile strength effect (TSE) [28,36]. The persistent appearance of this spike at exactly the same diameter after calcination at different temperatures was a proof of its artificial nature; however, it does not affect the assessment of the total mesopore volume.

While peak positions did not significantly change up to 500 °C in TTNT/A1 series (Fig. 8a–c), there was a clear shift of the main peak towards larger diameters already starting at 300–400 °C in TTNT/A2 series, suggesting again the least stability of TTNT/A2 samples. Despite the artifact in TTNT-A2/H, the observed tendency of shift in pore size distribution as a function of calcination temperature is a real trend. It is worth noticing that in TTNT-A2 series the shift of the first peak at 400 °C was not always accompanied by a reduction in the size of the peak (as noticed in TTNT-A1 series). Therefore, the collapse of the hollowed particles (nanotubes) might be occurring simultaneously to the growth of the solid nanoparticles. However, with further increase in calcination temperature, all the smaller pores (<10 nm) soon disappeared at 500 °C and the contribution of the large mesopores (10–60 nm) increased significantly due to the growth of the TiO₂ and Na₂Ti₅O₁₃ (Na₂Ti₃O₇ as well, at high Na loads) crystallites just like as occurred in TTNT/A1 series, although in this latter case starting above 500 °C. In any case, when the calcination temperature reached 800 °C, mesopore volume was reduced to almost zero due to effective sintering of the particles, which was confirmed by scanning electron microscopy.

Larger total mesopore volume and average pore diameter were observed in products of TTNT-A1 series in comparison with their counterparts of TTNT-A2 series (Fig. 9). With respect to these two parameters, the influence of
calcination temperature was quite similar in both A1 and A2 series, but apparently with some dependence on the sodium content. The total mesopore volume originally obtained with the as-synthesized TTNT seems to have been retained up to higher calcination temperatures, the higher the sodium content. Pore diameter increased steadily until a certain calcination temperature, above which an abrupt increase in mean pore diameter took place. This inflexion point due to nanoparticles growth occurred slightly earlier in TTNT-A2/M versus TTNT-A1/M, but not so evidently with the other two pairs (L and H).

Fig. 8. Pore volume distribution (BJH desorption) after calcination at increasing temperatures of the samples: (a) TTNT-A1/L; (b) TTNT-A1/M; (c) TTNT-A1/H; (d) TTNT-A2/L; (e) TTNT-A2/M; (f) TTNT-A2/H.
4. Conclusion

Multi-walled nanostructured trititanates with general formula Na\textsubscript{x}H\textsubscript{2-x}Ti\textsubscript{3}O\textsubscript{7-n}H\textsubscript{2}O were obtained via alkali hydrothermal treatment of different sources of TiO\textsubscript{2} anatase followed by water and/or acid washing procedure. When submitted to progressive heat treatment, these nanomaterials first release interlayer water and then transform into nanostructured hexatitanate causing significant reduction in the interlayer distance down to ca. 0.75 nm, just before further phase transformation into TiO\textsubscript{2}(B), TiO\textsubscript{2} anatase, Na\textsubscript{2}Ti\textsubscript{6}O\textsubscript{13} or mixtures thereof depending on the sodium content and calcination temperature. At high sodium loads (water washed materials), part of the nanostructured trititanate can be converted directly into larger crystals of Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} by-passing the intermediate hexatitanate nanostructure.

Fig. 9. Influence of calcination temperature on the total mesopore volume (a) and mean pore diameter (b) (BJH desorption) for the six TTNT samples. Calculated mean pore diameters of samples at 800°C were not reliable figures and were omitted.
The rate of phase transformation of TTNT into their calcined-derived forms turned out to be dependent on the crystallite size of the commercial TiO$_2$ anatase used as raw material for the synthesis reaction. Slightly faster transformation could be perceived for TTNT materials derived from starting anatase with smaller crystals. Thermal stability of TTNT samples could also be monitored through their textural properties, which revealed to be influenced by the type of starting anatase and by the sodium content. The modifications in pore size distribution with increasing calcination temperatures were tentatively rationalized in terms of collapse of nanotubes and growth of the resulting solid particles.

By proper selection of raw material and washing procedure as well as by controlling the calcination temperature it is possible to adjust the phase composition and textural properties of thermally treated nanostructured titanates.

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