Stability of Aqueous Suspensions of Titanate Nanotubes

Dmitry V. Bavykin,*,† Jens M. Friedrich,† Alexei A. Lapkin,‡ and Frank C. Walsh†

Electrochemical Engineering Group, School of Engineering Sciences, University of Southampton, Highfield, Southampton SO17 1BJ, U.K., and Catalysis and Reaction Engineering Group, Department of Chemical Engineering, University of Bath, Bath BA2 7AY, U.K.

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The long-term stability of titanate nanotubes, which were produced by alkaline hydrothermal treatment of TiO_2, was studied at room temperature in acidic, pure water, and basic aqueous suspensions. In pure water and basic (0.1 mol dm^{-3} NaOH) solutions, the nanotubes were stable and minimal morphological changes occurred. In 0.1 mol dm^{-3} H_2SO_4, suspended titanate nanotubes slowly transformed to rutile nanoparticles of ca. 3 nm size, which were agglomerated into ellipsoidal particles. The porosity, crystal structure, and morphology of protonated titanates and TiO_2 have been studied for intermediate states during the transformation by nitrogen adsorption, XRD, Raman spectroscopy, SEM, and HRTEM. The rate of conversion of nanotubes to nanoparticles has been related to the concentration of soluble titanium(IV) in solution, which depends on the nature of the acid. Thermodynamic and kinetic aspects of the acid transformation are discussed.

Introduction

Nanotubular titanium(IV) oxide materials, produced by alkaline hydrothermal treatment, are recently introduced[1] but intensively studied materials,[2,3] which are characterized by a nanosized diameter and unique physicochemical properties. These protonated titanate materials show promise for applications such as hydrogen sensors,[4] adsorbents,[5,6] photocatalysts,[7,8] mesoporous catalyst supports,[9−12] solar cell photosensitizers,[13] ion-exchange materials,[14−16] new generation electrodes for lithium batteries,[17,18] and electrocatalysts.[19,20] In many of these applications, titanate nanotubes can be exposed to chemically aggressive media.

Physically, titanate nanotubes are relatively fragile and can easily be broken up by mechanical forces during ultrasonic treatment,[21] resulting in shorter nanotubes. The thermal stability of titanate nanotubes has also been thoroughly studied and it was shown that during hydrothermal treatment in 0.1 mol dm^{-3} HNO_3 at 100 °C for 7 h, the titanate nanotubes can completely transform to anatase[14] and lose their tubular morphology. Annealing of the protonated form of titanate nanotubes in air at temperatures higher than 500 °C results in transformation of the nanotubes and formation of anatase having a fibrous morphology.[22] The sodium-saturated form of titanate nanotubes, however, is stable up to 850 °C.[14] Systematic studies of the phase transformation of titanate nanotubes at elevated temperatures during hydrothermal treatment have been reported recently[23] and it was demonstrated that both anatase and rutile polymorphs can be formed in the presence of nitric acid at temperatures higher than 80 °C after 48 h of treatment. The resulting anatase and rutile polymorphs had a fibrous or nanocrystalline morphology.

The successful application of titanate nanotubes requires data on the range of operational conditions under which

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[*] To whom correspondence should be addressed. Tel: +44 2380598752. Fax: +44 2380598754. E-mail: D.Bavykin@soton.ac.uk.

[†] University of Southampton.

[‡] University of Bath.

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nanotubes are stable. The knowledge of long term stability in various environments is extremely important for practical applications of titanate nanotubes. In this work, the stability of multilayered wall titanate nanotubes in the presence of 0.1 mol dm^{-3} bases and acids, at room temperature, was studied over a period of several months. During the acid transformation of nanotubes, all intermediate states were characterized. The correlation between the transformation of nanotubes to nanoparticles and the concentration of soluble titanium in solution (as Ti(IV)) has also been considered.

Experimental Details

Reagents. Titanium dioxide (anatase, TiO_2), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), hydrochloric acid (HCl), nitric acid (HNO_3), and hydrogen peroxide (27.5%, H_2O_2) pure grade were obtained from Aldrich and were used without further purification.

Preparation and Long-Term Stability Studies of "TiO_2" Nanotubes. The alkaline hydrothermal method of preparing titanate nanotubes was based on studies by Kasuga et al.[1] Nine grams of titanium dioxide (anatase) was added to 300 mL of 10 mol dm^{-3} NaOH solution in a PTFE beaker under vigorous stirring. The solution was placed in a PTFE-lined autoclave and heated for 22 h at 140 °C. The white, powdery titanates produced were thoroughly washed with water until the washing solution achieved pH 7 and then washed with 0.1 mol dm^{-3} H_2SO_4 on a glass filter for over 30 min followed by washing with water to pH 7. The sample was dried in a vacuum at 80 °C. The amount of sodium in produced nanotubes was not analyzed.

For the long-term titanate nanotube suspension aging studies, 0.2 g of nanotubes was placed in 9 vials and 10 mL of 0.1 mol dm^{-3} solution of NaOH, HCl, and HNO_3 was added. Ten milliliters of 0.1 mol dm^{-3} sulfuric acid was added to the five other vials. One vial was filled with 10 mL of distilled water. All vials were closed, ultrasonicated for 10 min, and kept at room temperature (22 ± 2 °C). After a controlled time, in the range from 5 days to 5 months, each sample was filtered, washed with water, and then dried in a vacuum at 80°C. The concentration of dissolved titanium in the filtered solution (0.2 μm nylon filter) was analyzed using the reaction with hydrogen peroxide. Ten milliliters of filtered solution was evaporated down to 1 mL; 0.1 mL of concentrated H_2SO_4 and then 1 mL of H_2O_2 were added. The concentration of Ti(IV) was determined, using a Shimadzu UV-1601 spectrophotometer, by measuring the characteristic band for absorption of the titanium peroxide complex at 420 nm.

Sample Characterization. The BET surface area and BJH pore distribution of the samples were measured, using nitrogen adsorption, on a Micromeritics ASAP 2010 instrument. TEM images were obtained using a JEOL 3010-TEM transmission electron microscope. SEM images were obtained with a JEOL 6500 FEG-SEM scanning electron microscope. XRD patterns were recorded using a Bruker AXS D8 Discoverer X-ray diffractometer, with Cu Kα radiation $\lambda = 0.154$ nm and a graphite monochromator, in the 2θ range of 5−50°. Raman spectra were recorded at room temperature (22 ± 2 °C) using a Renishaw 2000 spectrometer with HeNe laser ($\lambda = 632.8$ nm) excitation. Zeta potential measurements were obtained with a ZetaPlus Zeta Potential Analyser (Brookhaven Instruments Corporation) using the ZetaPals method. Zeta potential values were calculated using the Smoluchowski equation. Average electrophoretic mobilities were determined (10 cycles per run) in disposable plastic cuvettes (10 mm path length). The aqueous solutions were thoroughly deaerated with argon (Pureshield, BOC) prior to conducting experiments.

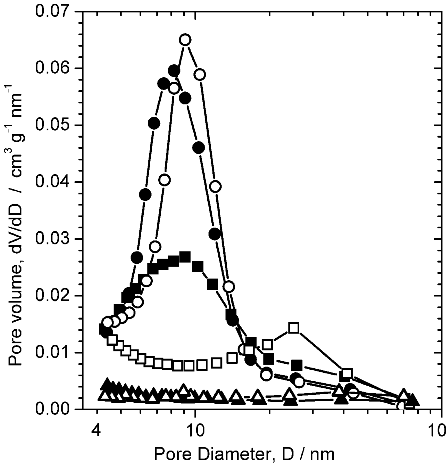

Figure 1. Pore volume distribution (BJH N_2 desorption) of titanate nanotubes soaked in 0.1 mol dm^{-3} H_2SO_4 for a controlled time at 22 ± 2 °C: (■) initial powder, (●) 5 days, (○) 15 days, (□) 32 days, (▲) 2 months, and (△) 5 months.

Results and Discussion

Ultradispersed nanoparticles, including many nanotubular materials, can be considered as thermodynamically metastable states, which can undergo further transformation into a more stable state in the absence of stabilizing factors.[24] The low solubility of inorganic oxide nanotubular materials in water suspensions is an important factor in kinetic stabilization during the process of aging when small particles dissolve and recrystallize to stable, massive crystals. Any increase in the rate of dissolution at higher temperatures or addition of chemical agents can facilitate the process of aging and decrease the stability of nanotubes. Strong acids and bases typically react with the surface of metal oxide powders, resulting in their modification. For example, in the case of photoactive anatase, treatment with sulfuric acid improves the activity of TiO_2 photocatalyst[25] without changing the crystal structure of particles; only the surface properties are modified. In contrast, it was found that treatment of titanate nanotubes in diluted sulfuric acid at room temperature for several months results in a complete change in particle morphology. In Figure 1, pore size distributions produced from a N_2 desorption curve using the BJH algorithm are shown for samples of nanotubular titanates treated with 0.1 mol dm^{-3} H_2SO_4 for controlled times. While the average pore size increases at longer times and there is a significant fall of BJH pore volume, V_{BJH} (see Table 1), the BET surface area, S_{BET} remains unchanged.

Figure 2 shows high-resolution SEM micrographs of the initial titanate nanotubes and rutile structures produced by aging nanotubes in 0.1 mol dm^{-3} H_2SO_4 for up to 5 months. Initial nanotubes (having an internal tube diameter ca. 3−5 nm, external diameter ca. 7−10 nm, and length of more than several hundreds of nanometers) slowly transform to ellipsoid particles having typical dimensions of 50 × 200 nm. These particles consist of smaller particles of rutile nanocrystallites. In the intermediate stages (Figure 2b) nanotubes and rutile nanoparticles coexist.

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Table 1. Change of Titanate Nanotube Properties during Slow Transformation in Acids and Alkali

solution	time of treatment	S_{BET}[a] ($m^2 g^{-1}$)	V_{BJH}[b] ($cm^3 g^{-1}$)	zeta potential (mV)	concentration of Ti(IV)[c] (mmol dm^{-3})
H_2O	0 day	199	0.70	−42.7	3×10^{-3}
0.1 mol dm^{-3} H_2SO_4	5 days	240	0.69	6.6	0.65
0.1 mol $dm^{-3}$$H_2SO_4$	15 days	251	0.69	6.6	0.65
0.1 mol dm^{-3} H_2SO_4	32 days	235	0.64	n/a	0.65
0.1 mol dm^{-3} H_2SO_4	2 months	184	0.25	n/a	0.65
0.1 mol dm^{-3} H_2SO_4	5 months	246	0.30	n/a	0.65
0.1 mol dm^{-3} NaOH	5 months	161	0.56	−36.7	0.22[d]
0.1 mol dm^{-3} HCl	2 months	247	0.73	n/a	0.25
0.1 mol dm^{-3} HNO_3	2 months	199	0.55	n/a	0.35

[a] S_{BET} is the specific surface area of powder. [b] V_{BJH} is the cumulative pore volume determined from the desorption curve. [c] The concentration of Ti(IV) was measured after 2 months of treatment at room temperature.[d] The concentration was extrapolated form high temperature to room temperature using eq 5 from reference 21 and the value of enthalpy of dissolution = 23 kJ mol^{-1}.

The early stages of titanate nanotube dissolution in dilute sulfuric acid, at room temperature, have been investigated by means of high-resolution transmission electron microscopy (Figure 3). The original, well-defined, multilayered wall crystal structure of the titanate nanotubes (Figure 3a) is distorted, even after 5 days of room-temperature treatment with 0.1 mol dm^{-3} H_2SO_4 (Figure 3b). This results in the disappearance of the multilayered structure of nanotube walls and corrosion of the surface. The walls of nanotubes became thinner and the specific surface area is increased. After 2 months of acidic treatment, nanotubular structures disappear completely and TiO_2 rutile nanoparticles of average size ca. 3 nm are formed. The crystal structure of rutile nanoparticles is well-defined with an interplanar distance between 110 planes of ca. 0.33 nm (see Figure 3c). These rutile nanoparticles agglomerate to form secondary particles of ellipsoid shape (see Figure 3d). The specific surface area of this rutile sample is relatively high, making such TiO_2 samples interesting for various applications. Indeed, the conventional way of producing rutile is annealing at very high temperature, which results in sintering of nanoparticles and decrease in surface area. Such a high-temperature treatment eliminates surface OH groups, changing the chemistry of the surface. In contrast, very slow acid-assisted transformation of titanate nanotubes to TiO_2 rutile nanoparticles could be a promising method for producing rutile nanoparticles.

Despite some debate over the crystal structure of titanate nanotubes between the following structures, $H_2Ti_3O_7$,[26] $H_2Ti_2O_4(OH)_2$,[15] $H_2Ti_4O_9{\cdot}H_2O$,[27] or monoclinic TiO_2−B,[16] we denote here the apparent pattern of initial nanotubes (see Figure 4a) as trititanic acid, $H_2Ti_3O_7$, having characteristic 2θ reflections of 9.5, 11.2, 24.4, 29.0, 37.9, and 48.4°. Long-term washing of the nanotubes with sulfuric acid resulted in complete disappearance of the trititanic acid phase, accompanied by the appearance of the rutile phase having characteristic reflections at 27.5, 36.1, 41.3, and 44.1°. The coherence area for the rutile crystals was calculated from the half-width at half-height of the (110) plane diffraction peak ($2\theta = 27.5°$) using the Scherrer equation and was found to be approximately 3.9 nm for samples (e) and (f) in Figure 4, in agreement with HRTEM results. The sample produced after 32 days of immersion in sulfuric acid was an approximately equimolar mixture of nanotubular $H_2Ti_3O_7$ and rutile. In all of the samples, the amount of anatase phase is negligible. It is interesting to note that even short-term acid treatments result in the disappearance of characteristic reflection at 10.2° (see Figure 4b), which is related to the layered structure of the nanotube walls. This observation is in agreement with TEM data (see Figure 3b), indicating that multilayered structure of nanotube wall vanishes after 5 days of acid treatment.

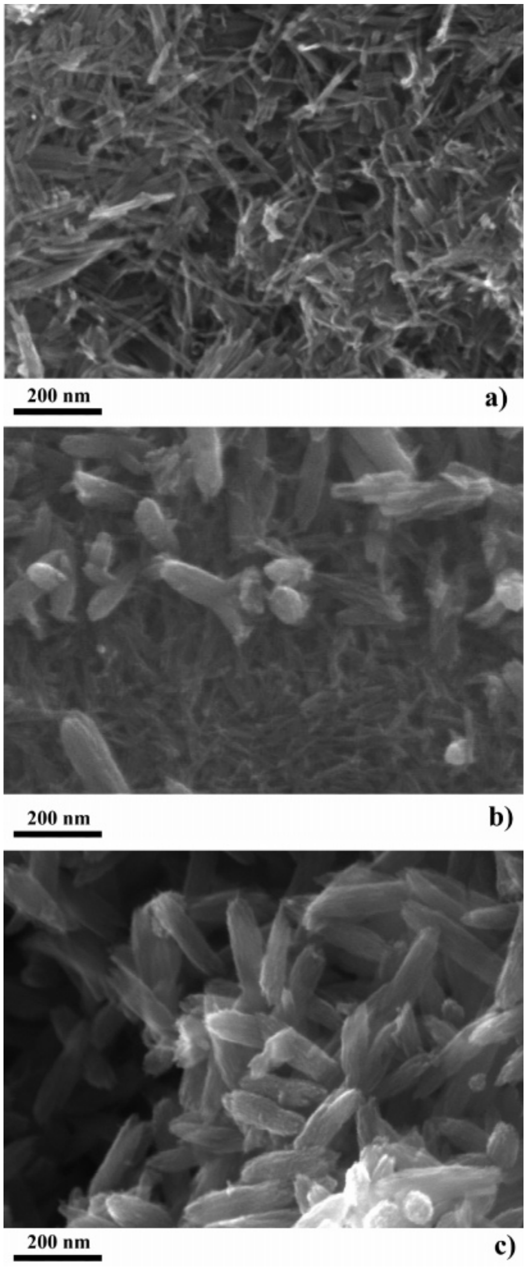

Figure 2. HRSEM pictures of protonated titanates and TiO_2 (a) initial nanotubes, (b) nanotubes partially transformed to rutile nanoparticles after 32 days of aging in 0.1 mol dm^{-3} H_2SO_4 at 22 ± 2 °C, and (c) nanotubes completely transformed to rutile nanoparticles after 2 months of aging in 0.1 mol dm^{-3} H_2SO_4 at 22 ± 2 °C.

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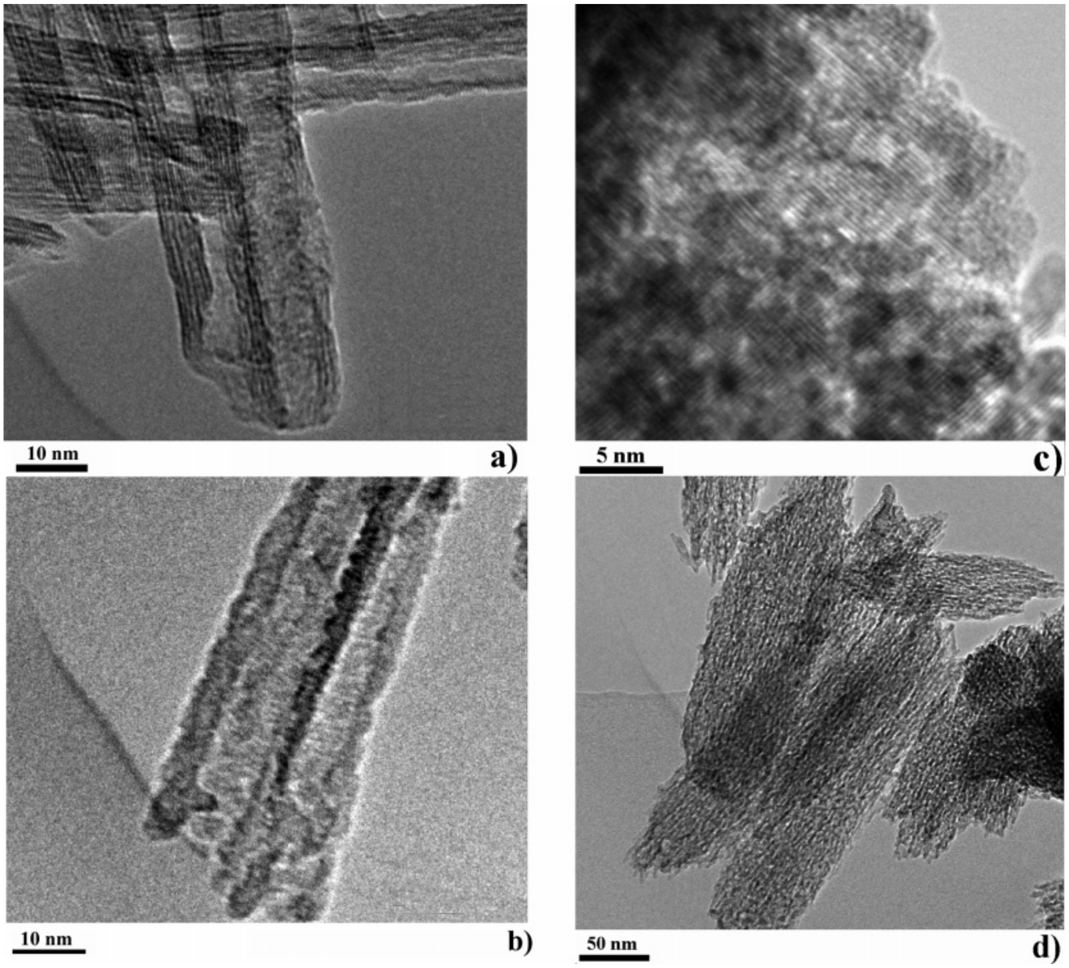

Figure 3. HRTEM images of protonated titanates and TiO_2 (a) initial nanotubes, (b) corroded nanotubes after 5 days of aging in 0.1 mol dm^{-3} H_2SO_4 at 22 ± 2 °C, and (c) and (d) nanotubes transformed to rutile nanoparticles after 2 months of aging in 0.1 mol dm^{-3} H_2SO_4 at 22 ± 2 °C.

Previously, it has been reported[28] that SO_4^{2-} ions in solution stimulate the preferential formation of the anatase phase of TiO_2 during hydrolysis reactions. In our case, the presence of sulfate ions during the transformation of nanotubes did not promote the anatase phase formation. In general, the formation of the rutile phase at room temperatures is relatively rare. Adding relatively concentrated 1 mol dm^{-3} HCl or HNO_3 can promote recrystallization of amorphous TiO_2 to rutile at room temperature.[29] Addition of sulfuric acid, however, results in the formation of anatase. Phase transformation of protonic layered titanates $H_2Ti_4O_9$ to the anatase TiO_2 in water suspension begins at 225 °C without the formation of a rutile phase.[30] We believe that the rate of TiO_2 recrystallization affects the crystal structure of the produced polymorph. Lower rates result in a higher probability of formation of the thermodynamically stable and symmetrical rutile phase. Indeed, in all our experiments on phase transformation of titanate nanotubes, the time of complete transformation exceeded several months. When the rate of recrystallization was increased by the addition of concentrated acid[28] or increased temperature,[30] the probability of anatase phase formation was higher.

Sulfuric-acid-assisted, room-temperature transformation of titanate nanotubes to the rutile nanoparticles is also accompanied by changes in the Raman spectrum (Figure 5). The initial sample of titanate nanotubes (Figure 5a) has two sharp and intensive lines at 290 and 448 cm^{-1}, one multiple line centered at 668 cm^{-1} and several less intensive lines at 388, 827, and 917 cm^{-1}. This spectrum is similar to the recently observed spectrum of titanate nanotubes[14,31,32] and could not be superimposed onto Raman spectra of anatase and rutile. The exact assignment of these peaks is still under dispute but they could be interpreted as Ti−O−Ti crystal phonons (more likely for 448 and 668 cm^{-1} peaks), Ti−O−Na vibrations (more likely for 917 cm^{-1} peak), second-order harmonics, or radial "breathing" oscillations intrinsic to nanotubular structures.[33] Remarkably, after 5 days acid treatment of titanate nanotubes, a widening of the 448 cm^{-1} peak, shifting of the 668 cm^{-1} peak to the smaller energy, and a lowering of all other peaks occur (see Figure 5b). At the same time, the morphology of the sample is still

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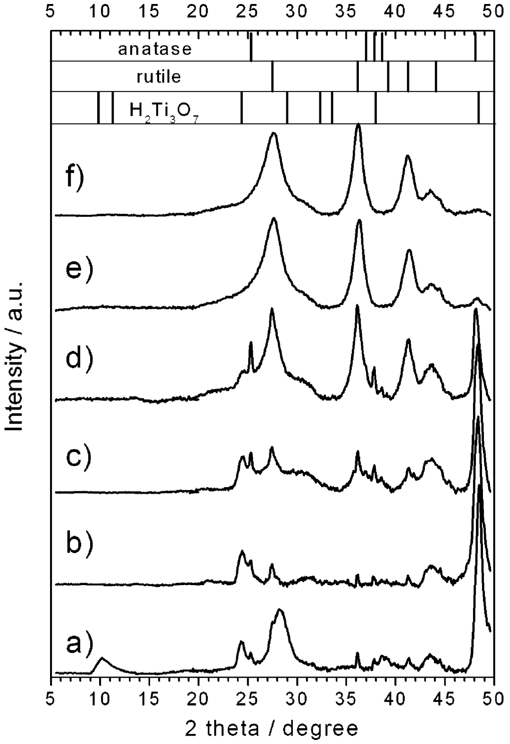

Figure 4. Powder XRD patterns of titanate nanotubes and acid-washed samples for different times at 22 ± 2 °C: (a) initial sample; (b) 5 days; (c) 15 days; (d) 32 days; (e) 2 months; (f) 5 months. Rutile, anatase, and $H_2Ti_3O_7$[26] reflections are shown as line patterns. The curves are shifted vertically for clarity.

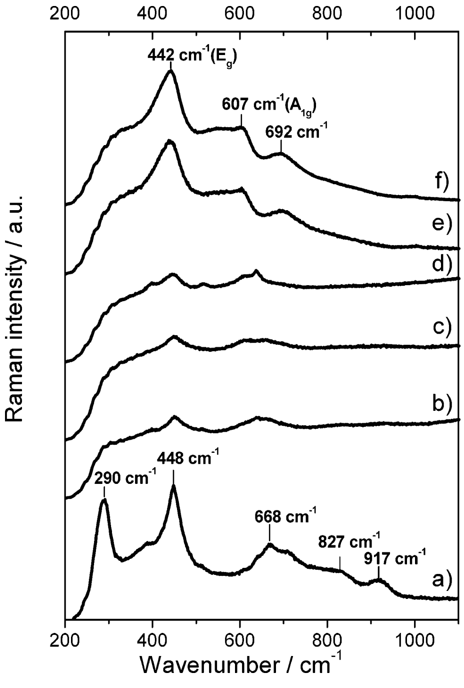

Figure 5. Raman spectra of titanate nanotubes and acid-washed samples for different times at 22 ± 2 °C: (a) initial sample; (b) 5 days; (c) 15 days; (d) 32 days; (e) 2 months; (f) 5 months. The baseline was not subtracted. The curves are shifted vertically for clarity.

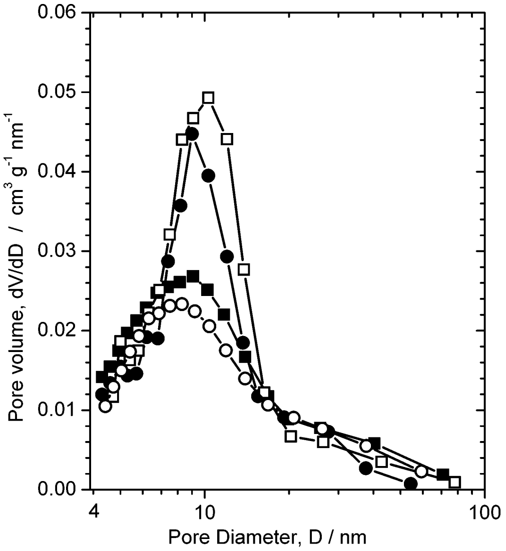

Figure 6. Pore volume distribution (BJH N_2 desorption) of titanate nanotubes immersed in various 0.1 mol dm^{-3} aqueous solutions at 22 ± 2 °C: (■) initial powder; (●) after 2 months in HNO_3; (○) after 5 months in NaOH; (□) after 2 months in HCl.

nanotubular (see Figure 3b) and its XRD pattern is still very similar to that of the $H_2Ti_3O_7$ (see Figure 4b). The disappearance of the 917 cm^{-1} peak could be explained by the ion exchange of Na^+ to H^+ in acid solution. The disappearance of the 290 cm^{-1} peak, however, is probably due to the other reasons since it was demonstrated recently that ion exchange does not change the position and intensity of this peak.[34] The Raman spectra of 2 and 5 months acid-treated samples show several wide peaks, which correspond to the Raman active phonons of rutile: 442 cm^{-1} (E$_g$), 607 cm^{-1} (A$_{1g}$), and 692 cm^{-1}.[35] These active phonon transitions are also detected in the intermediate states (Figures 5c and 5d).

Data on the stability of a suspension of titanate nanotubes in 0.1 mol dm^{-3} solutions of HCl or HNO_3 are shown in Figure 6 and Table 1. Aging of titanate nanotubes for 2 months in HCl and HNO_3 results in the partial transformation of nanotubes. The pore size distribution of nanotubes aged for 2 months in HNO_3 and HCl was similar to the pore size distribution of nanotubes aged in H_2SO_4 for several days. Consequently, the rate of titanate nanotube transformation in 0.1 mol dm^{-3} solution of HCl and HNO_3 was several times less than the rate of transformation in H_2SO_4. Such a difference in reaction rate can be correlated with the solubility of titanate nanotubes in different acids. It was found that the concentration of the soluble form of Ti(IV) in an acid suspension of titanate nanotubes depends on the nature of the acid and decreases in the order $H_2SO_4 > HNO_3 \approx HCl$. The use of higher concentrations of Ti(IV) during the dissolution of nanotubes resulted in a faster nanotube to nanoparticle transformation. This confirms that the mechanism of acid-assisted transformation includes partial dissolution of nanotubes accompanied by the release of soluble Ti(IV), which is crystallized to nanoparticles of rutile.

In pure water suspensions, no phase transformation of nanotubes was detected. The concentration of soluble Ti(IV) above titanate nanotubes at room temperature is very small and probably includes an error resulting from the existence of short colloidal nanotubes, which were formed because of the breaking of long nanotubes during ultrasonic treatment[21] and which passed through the 0.2 μm filter. In

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contrast, the concentration of Ti(IV) in 0.1 mol dm^{-3} solutions of NaOH (see Table 1) estimated by extrapolation of concentration at high temperature is similar to the concentration of Ti(IV) in diluted hydrochloric acid. However, the studies of the effect of base solution on the stability of titanate nanotubes suspension have revealed that there was no significant change in pore size distribution, surface area, or pore volume for samples aged for 5 months in NaOH solution. This means that, in basic solution, titanate nanotubes are thermodynamically stable. Indeed, the high concentration of dissolved Ti(IV) would provide the route for transformation of titanate nanotubes to the stable form of TiO_2. The high pH and high sodium ion level in the solution probably favor the layered sodium titanate phase, which stabilizes the multilayered wall titanate nanotubes. The initial titanate nanotubes are also produced during alkaline hydrothermal treatment, suggesting that basic conditions stabilize the titanate nanotubes.

The value of the zeta potential of protonated titanate nanotubes aqueous suspension could also be a key factor in initiating the process of transformation. Since nanotubular trititanic acid is a weak acid[12] in water, the following dissociation can occur:

$$(H_2Ti_3O_7)_s \leftrightarrow (HTi_3O_7)^-{}_s + H^+ \tag{1}$$

This results in a negative zeta potential in water (see Table 1). The addition of NaOH slightly increases the potential due to the adsorption of sodium ions.[14,15] In contrast, addition of 0.1 mol dm^{-3} sulfuric acid results in shifting the equilibrium (1) to the left and significantly increases the zeta potential, leading to a change of sign for the surface charge, the zeta potential having a small positive value. Excess adsorption of protons from solution onto the surface of nanotubular titanates can destabilize the crystal structure of the multilayered trititanic acid, resulting in leaching of the surface TiO_6 octahedra.

Thus, the sequence of events during acid-assisted phase transformation of titanate nanotubes at room temperature can be considered via the three following steps. Within the first few days, the layered wall structure of nanotubes is disrupted, the surface of nanotubes is eroded, and long order in crystal structure is partially disturbed, resulting in a decreasing intensity of some reflections in the XRD and the disappearance of some Raman active phonon transitions; the morphology of nanostuctures is still tubular and titanium is still in the form of trititanic acid $H_2Ti_3O_7$. The longer acid treatment resulted in the appearance of rutile nanoparticles agglomerated in to the ellipsoid shape secondary particles and disappearance of the trititanic phase. In this intermediate state, both phases coexist. In the final stage, after several months of acid treatment, a very slow recrystallization of trititanic acid results in the formation of the most stable (rutile) phase of TiO_2 nanoparticles.

Conclusions

1. The long-term stability of titanate nanotubes in acidic, basic, and pure water suspensions was studied. It was demonstrated that in basic solution nanotubes are thermodynamically stable and in water suspension nanotubes are kinetically stable. In both cases, in water or basic (0.1 mol dm^{-3} NaOH) solutions, the titanate nanotubes are stable and undergo minimal morphological changes.

2. In dilute sulfuric acid (0.1 mol dm^{-3} H_2SO_4) suspended titanate nanotubes are neither thermodynamically nor kinetically stable. They slowly transform to rutile nanoparticles of 3 nm size agglomerated to the globules of ellipsoid morphology.

3. In 0.1 mol dm^{-3} solutions of HCl and HNO_3 the process of transformation is several times slower and the concentration of soluble Ti(IV) is also several times lower than in 0.1 mol dm^{-3} H_2SO_4, confirming that the mechanism of acid-assisted transformation includes dissolution of nanotubes, release of soluble forms of Ti(IV) in solution, and crystallization of dissolved Ti(IV) to rutile nanoparticles.

4. Nitrogen adsorption, XRD, Raman spectroscopy, SEM, and HRTEM studies of intermediate states have revealed that, in the beginning of acid-assisted transformation, the nanotubular morphology is maintained, whereas the crystal structure of trititanic acid $H_2Ti_3O_7$ is disrupted. Following transformations result in the appearance of rutile nanoparticles and the disappearance of nanotubular $H_2Ti_3O_7$.

5. The final TiO_2 rutile nanoparticles, produced by slow recrystallization of nanotubes in acids, have a high specific surface area (BET N_2 adsorption) of 246 ± 7 m^2 g^{-1}.

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