Systematic evaluation of thermal and mechanical stability of different commercial and synthetic photocatalysts in relation to their photocatalytic activity

S. Ribbens, E. Beyers, K. Schellens, M. Mertens, X. Ke, S. Bals, G. Van Tendeloo, V. Meynen, P. Cool

Abstract

The effect of thermal treatment and mechanical stress on the structural and photocatalytic properties of eight different (synthetic and commercial) photocatalysts has been thoroughly investigated. Different mesoporous Ti-based materials were prepared via surfactant based synthesis routes (e.g. Pluronic 123, CTMABr = Cetyltrimethylammonium bromide) or via template-free synthesis routes (e.g. tititanate nanotubes). Also, the stabilizing effect of the NaOH/NH4OH post-treatment on the templated mesoporous materials and their photocatalytic activity was investigated. Furthermore, the thermal and mechanical properties of commercially available titanium dioxides such as P25 Evonik and Millenium PC500 were studied. The various photocatalysts were analyzed with N2-sorption, X-ray diffraction (XRD), high resolution transmission electron microscopy (HR-TEM), differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) to obtain information concerning the specific surface area, pore volume, crystal structure, morphology, phase transitions, etc. In general, results show that the NaOH post-treatment leads to an increased control of the crystallization process during calcination resulting in a higher thermal stability, but at the same time diminishes the photocatalytic activity. Mesoporous materials in which pre-synthesized nanoparticles are used as titania source have the best mechanical stability whereas the mechanical stability of the nanotubes is the most limited. At increased temperatures and pressures, the tested commercial titanium dioxides lose their superior photocatalytic activity caused by a decreased accessibility of the active sites. The observed changes in adsorption capacities and photocatalytic activities cannot be assigned to one single phenomenon. In this respect, it shows the need to define a general/standard method to compare different photocatalysts. Furthermore, it is shown that the photocatalytic properties do not necessarily deteriorate under thermal stress, but can be improved due to crystallization, even though the initial material is (partially) destroyed. It is shown that the usefulness of a specific type of photocatalyst strongly depends on the application and the temperature/pressure to which it needs to resist.

1. Introduction

Environmental standards (ISO 14001, October 1996) are becoming more stringent. Therefore, a wide variety of technology was developed (adsorption [1,2], biodegradation [3], ozonation [4,5], Fenton reactions [6]…) for the removal of organic pollutants present in air- and water streams. Among these techniques, heterogeneous photocatalysis has appeared to be very promising. Indeed, photoinduced “advanced oxidation processes” (AOP) can lead to a complete mineralization of most organic pollutants, like dyes and aromatic hydrocarbons, that are emitted by industrial and domestic activities [7,8]. Therefore, semiconductor photocatalysis became an established, significant and still expanding area of research [9–11]. Titanium dioxide has been proven to be the most efficient photocatalyst for the degradation of harmful pollutants in water and air [12–15]. Although, commercial available titanium dioxide powders (e.g. P25 Evonik, TiO2 Riedel-De-Haen, Millenium PC500) show high photocatalytic efficiency, these nanocrystalline titania powders have often a low surface area and are often hard to recover out of solution due to their small particle sizes. Therefore, up till now, the number of industrial applications...
2.1.1. Chemical reagents

2. Experimental section

Performances, available and newly developed photocatalysts in relation to their respective investigations on the thermal and mechanical stability of other labscale based on templated and template free synthesis routes).

This study shows the need and forms a basis for further comparison/systematic information concerning their thermal and mechanical stability. Besides thermal stability, also the mechanical stability of the photocatalyst is of importance to (1) avoid a collapse of the structure during calcination, necessary to remove the organic template in mesoporous photocatalysts [16]. (2) The structure needs to withstand high calcination temperatures in order to induce (re)crystallization which is crucial in various cases (e.g. mesoporous photocatalysts) to enhance the photocatalytic activity [27, 28]. Besides thermal stability, also the mechanical stability of the photocatalyst is essential. Indeed, if the production process reaches an industrial level, it should be possible (1) to store the catalyst in high silos or warehouses without changing the characteristics of the material under the mechanical stress, (2) to allow formulation of the synthesized powders into pellets, extrudates, etc. which are for example required to facilitate separation from aqueous medium and (3) to withstand water pressures or vapor streams in purification plants. Although the thermal [29–31] and mechanical stability [32–34] of different titanias based materials have already been studied, the various stability tests are often incomplete and performed under different conditions. This variation makes it difficult to make a systematic comparison between the different photocatalysts with respect to performance and stability of these materials. Therefore, in this study, the thermal and mechanical (unilateral pressure) limitations of the best known commercial and synthetic photocatalysts are studied. It is the first systematic and comparative study of the thermal and mechanical stability in relation to the photocatalytic activity of a total of eight different Ti-based photocatalysts (commercially available or prepared at labscale based on templated and template free synthesis routes). This study shows the need and forms a basis for further comparative investigations on the thermal and mechanical stability of other available and newly developed photocatalysts in relation to their performances.

2.1.2. Templated synthesis and post-treatment

For the synthesis of mesoporous titanium dioxide, two different templated synthesis strategies were applied.

The Evaporation Induced Self Assembly (EISA) method is a common applied method for the synthesis of mesoporous transition metal oxide materials [16, 35]. A first solution was prepared by dissolving 2.36 g (CTMAB) in 24 mL ethanol. In a second solution 22.80 mL EtOH, 4.7 mL HCl and 12.00 mL of Ti(OiPr)4 were mixed. These two mixtures were stirred and added to each other, followed by the addition of 8.2 mL of H2O. After 1 h of stirring, the solution was transferred into a Petri dish and dried in an oven for 1 week at 60 °C.

Kartini-method: Instead of using a molecular Ti-precursor, pre-synthesized anatase nanoparticles are being used as titania source [16, 36]. Therefore, 5 mL Ti(OiPr)4 was added to a mixture of 6.6 mL H2O and 10 mL EtOH. The mixture was stirred at room temperature for 2 h and hydrothermally treated at 80 °C for 4 h in a Teflon lined autoclave. The formed nanoparticle solution was quenched and added to an aqueous solution of Pluronic 123 (3.2 g EO20PO70EO20 in 40 mL H2O). This suspension was stirred for 1 h at 40–50 °C, followed by a hydrothermal treatment in a Teflon lined autoclave at 100 °C for 20 h. After quenching and filtration, the samples were washed 3 times with 25 mL H2O.

Stabilization: In order to stabilize the mesoporous structures during calcination, samples (both EISA and Kartini) were post-treated by refluxing 1 g of solid in 50 mL of a basic, aqueous solution of NaOH or NH4OH for a period of 48 h (the reflux temperature is that of the aqueous solution (~100 °C) [16]. NaOH treatment took place in a 0.112 M NaOH solution. For the NH4OH post-treatment, the pH was kept constant between 9 and 10 by addition of NH4OH (Acros 28–30% p.a.) to the solution.

2.1.3. Template free synthesis

Trititanate nanotubes (TNT) are rolled-up mesoporous materials, prepared without addition of templates [25, 35, 37, 38]. Here, 4.5 g TiO2 Riedel-de-Haën® (anatase powder, 12 m2/g) was dispersed into 80 mL of 10 M NaOH solution under vigorous stirring during 1 h. The mixture was transferred into an autoclave and hydrothermally treated at 150 °C for 48 h. After hydrothermal treatment, the solid was recovered by centrifugation. The precipitate was washed three times with deionized water. In this way, sodium trititanate nanotubes are obtained. The sodium nanotubes can be ion-exchanged to hydrogen trititanate nanotubes by acid washing. Therefore, Na-TNT was dispersed in 240 mL 0.1 M HCl and stirred for 30 min. The solid was recovered by centrifugation and dried for 2 days. Afterwards, the dried powder was dispersed again in 100 mL 0.1 M HCl and stirred for 5 min. The precipitate was separated by filtration and washed three times with water. Finally, the washed solid was dried at 100 °C for several days.

2.2. Characterization

The surface area and porosity of the prepared materials were determined via N2-sorption on a Quantachrome Quadrasorb SI automated gas adsorption system. H-TNT and Na-TNT were outgassed at 150 °C and Millenium PC500 was degassed at 100 °C to prevent structural changes upon degassing. All the other described samples were outgassed at 200 °C for 16 h. After degassing, N2-sorption was carried out at –196 °C. The Brunauer–Emmett–Teller (BET) method was applied to calculate the specific surface area. The pore size distribution was calculated from the adsorption branch using the Barret–Joyner–Halenda (BJH) model. The volume adsorbed at a relative pressure P/P0 = 0.98 was applied to determine the total pore volume. The error on each measurement is around 5–10%, which has to be taken into account, especially when the determined surface areas are low.

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X-ray diffraction patterns (XRD) were collected on a Panalytical XPert PRO MPD diffractometer using CuKα radiation in 2θ mode with a bracket sample holder. Measurements were done at a scanning speed of 0.04°/4s continuous mode. The crystal sizes of anatase were calculated via the Scherrer equation.

By performing electron energy loss spectroscopy (EELS), the crystallinity of the as-prepared samples was determined. Reference spectra of trititanate and amorphous TiO2 were recorded. All the reference signals have been background subtracted, deconvoluted and normalized. The spectra for the samples were then interpreted as a linear combination of the two references spectra, taking into account a background and multiple scattering. The use of EELS for the determination of crystal and amorphous phase compositions has been described in detail in a previous paper [39].

The amount of sodium in the NaOH treated samples was determined with electron probe micro analysis (EPMA, JEOL JXA 733 superprobe).

Using Scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HR-TEM), the morphology of the samples could be examined. HR-TEM pictures were taken on a Philips CM30 at 300 kV. Low beam intensities were applied in order to preserve the structure. SEM was performed using a JSEM 5510 system. The samples were sputtered with a thin film of gold to minimize the charging effects. Differential scanning calorimetry (DSC) gave information about the thermal stability of the samples, their composition and possible phase transformations. The measurements were performed on a SDT2960 module (TA-instruments). Samples were heated at a heating rate of 5 °C/min under N2 atmosphere (flow rate of 50 cm3/min) up to 800 °C.

2.3. Photocatalysis

The photocatalytic activity was tested by photodegradation of an artificial cationic pollutant (rhodamine-6G = R6G or pyridine chloride = PyCl) in aqueous solution. The catalyst (8 mg of EISA/Kartini, 16 mg of H-TNT/Na-TNT or commercial catalyst) was added to a suspension of 50 mL dye solution and stirred in dark in order to establish an adsorption–desorption equilibrium between the dye molecules and the catalyst surface. The stirring speed was adjusted in such a way that the catalyst remained well dispersed in the solution. The stirring speed was kept constant in all experiments. A large magnetic stirrer was applied in order to assure a good dispersion of the catalyst.

After establishing equilibrium, the solution was irradiated for 60 min with UV light (wavelength 365 nm) emitted by a 100 Watt Hg-lamp (Sylvania Par 38; 21.7 mW/cm2 at 5 cm). The distance between the pollutant solution and the UV-lamp is fixed. During this illumination, samples with a volume of 5 mL were taken out of the suspension at fixed time intervals (10 min) and analyzed by UV–Vis spectroscopy (Thermo-electron evolution 500, double beam UV–Vis spectrometer) and brought back to the pollutant solution after analysis. The absorbance was measured at 526 nm (R6G) or at 256 nm (PyCl) with water as a reference. The dissolved oxygen demand was measured by an oxygen electrode and determined at 350 °C. The temperature was then increased in steps of 100 °C in a Lenton furnace under ambient conditions with a heating ramp of 1 °C/min. The desired temperature was kept constant for 6 h. Further increase in heating was done up to the point where a complete collapse of the structure was observed (chosen by the authors as less than 50% of the original SBET).

2.4. Thermally induced mineralization

The photobleaching process (UV) was analyzed for a period of 60 min, total organic carbon analysis was performed for 120 min in order to have more detailed information on the photomineralization capacity of the different catalysts [40]. All described values of adsorption, photodegradation and total conversion (= sum of adsorption and photodegradation) have been obtained by subtracting the measured concentration of the pollutant/dye in solution at a given time from the initial pollutant/dye concentration (PyCl of R6G) in solution before adsorption (adsorption and total conversion: stock solution) or at adsorption–desorption equilibrium (photodegradation: 0 min, the moment the UV-light is put on the sample).

Blanc measurements have been performed (not shown) to ensure that all observed effects were true photocatalytic degradation reactions. Photolysis of R6G and PyCl only takes place after a period of 5 h or longer which is much longer than the experiments described herein.

2.4.1. Thermal stability

To study the thermal stability of the templated mesoporous materials, the samples were heated. A temperature of 450 °C was taken as starting temperature in order to assure complete removal of the template. In case of template free mesoporous photocatalysts (Na-TNT and H-TNT), the thermal stability tests were started at 350 °C. The temperature was then increased in steps of 100 °C in a Lenton furnace under ambient conditions with a heating ramp of 1 °C/min. The desired temperature was kept constant for 6 h. Further increase in heating was done up to the point where a complete collapse of the structure was observed (chosen by the authors as less than 50% of the original SBET).

2.4.2. Mechanical stability

Mechanical tests were performed by pelleting the samples into a disc with a diameter of 13 mm. The pressure was increased in steps of 740 MPa and was kept constant for 2 min. After pelleting the samples, the discs were softly ground by hand in a mortar, resulting in a fine powder.

All materials will be regarded as completely degraded if more than 50% of the initial surface area is lost due to thermal treatment or mechanical pressure.

3. Results and discussion

3.1. Thermal stability

3.1.1. Templated materials synthesized via the Kartini and EISA method

The as-prepared Kartini and EISA samples which are post-treated by refluxing in an aqueous NaOH or NH4OH solution will be
respectively referred to as “EISA TNaOH, EISA TNH4OH, Kartini TNaOH and Kartini TNH4OH”. The non-treated samples will be indicated by respectively “EISA nT” and “Kartini nT”. In Table 1, the surface areas, total pore volumes and crystal sizes of the non-treated and alkaline post-treated EISA and Kartini samples are plotted as function of the applied calcination temperature. It can be observed that the Kartini samples are characterized with smaller surface areas as compared to the EISA samples (e.g. Kartini TNaOH C450: 136 m²/g and EISA TNaOH C450: 383 m²/g). Beyers et al. [16] assigned the lower mesoporosity of the Kartini samples to the limited interaction between the pre-synthesized anatase nanoparticles and the surfactant. The alkaline post-treatments are applied in order to preserve the structure during calcination by controlling the crystal growth [16,41,42]. Indeed, as observed in Table 1, excessive crystal growth of the untreated EISA nT and Kartini nT samples results in a complete loss of the mesoporous structure at 550 °C (loss of more than 50% of the initial surface area). Although the structure of both the EISA and Kartini sample completely collapse at 550 °C, it can be seen that the Kartini sample is characterized by a higher thermal stability. Indeed, at 450 °C, the surface area of EISA nT diminished with 68% whereas a decrease of only 24% is observed for Kartini nT. The use of pre-synthesized anatase nanoparticles in Kartini nT materials during synthesis in contrast to the absence of measurable crystals for the EISA samples, results in internal stabilization [43].

Due to the low thermal stability of the untreated materials, only the alkaline post-treated samples will be further discussed. Considering the EISA samples, it can be seen that 53% of the initial surface of EISA TNaOH is lost after calcination at 650 °C compared to a surface loss of 48% for EISA TNH4OH. It is clear that both post-treatments have the same efficiency towards the thermal stability of the EISA sample. However, clear differences between the post-treatments can be observed for the Kartini method: the loss of surface area of the NaOH treated Kartini sample after calcination at 650 °C (28%) is much less compared to the NH4OH treated Kartini sample (53% at 650 °C). Considering the crystal growth of the Kartini samples at elevated temperatures (see Table 1), it is clear that the NaOH post-treatment allows for a better inhibition of uncontrolled crystallization during thermal treatment (6 nm at 650 °C) as compared to NH4OH (11 nm at 650 °C). Indeed, the presence of NaOH ions on the surface after post-treatment (~3 wt% Na; measured with EPMA) limits the crystallization and growth of anatase during calcination as described by Nam [43,44]. The fact that this post-treatment is not as effective for the EISA samples as it is for the Kartini samples, although crystal growth is efficiently controlled, indicates that other phenomena play an additional role like for instance porosity, wall thickness, degree of crystallinity, presence of anatase nanoparticles,… Therefore, it is difficult to predict the stability of the developed catalysts. From the above results it is clear that a general method to stabilize different materials is difficult to find and every stabilization method needs to be adapted to the type of material and synthesis method. Furthermore, it shows the importance of this systematic study and the lack of nuances in literature.

Fig. 1 shows the effect of crystallization, post-treatment and loss of available surface area on the adsorption capacity and photocatalytic activity in function of the calcination temperature. It can be seen that the adsorption capacity of the NaOH post-treated EISA sample decreased by 47% after calcination at 650 °C (Fig. 1A). This decrease coincides with the observed loss in surface area (53%) (see Table 1). Although, EISA TNH4OH C650 has a similar loss in surface area after increasing the temperature from 450 to 650 °C (48%), the adsorption capacity isn’t affected by this decrease. The same trend can be observed for the NH4OH treated Kartini samples (Fig. 1B). It is clear that the NH4OH treated samples have a lower adsorption capacity in general, however it is much more thermally stable. This points to the influence of other, multiple material characteristics other than surface area such as crystallinity, accessibility and diffusion/mass transport, particle sizes and distribution, surface adsorption kinetics etc. that need to be taken in account to unravel the influence of thermal stability on the adsorption capacity. For example, a stronger increase in crystallinity has taken place for the NH4OH post-treated samples as compared to the NaOH treated samples, which can be observed by the increase in intensity of the anatase diffraction peaks with increasing temperature in XRD. The diffraction peaks remain broad confirming that no strong crystal growth takes place (Fig. S1 and Table 1). Whereas amorphous TiO2 shows only a short-range order and a lot of structural defects (large amount of under- or overcoordinated structural Ti-units and dangling bonds) [44], the anatase phase has a well formed lattice with a small amount of structural defects and high amount of hydroxyl groups which results in higher adsorption capacities [45,46]. However, this effect does not explain all observed differences in thermal stability. It needs to be noted that by comparing the NaOH and NH4OH post-treated samples, it becomes clear that the NaOH treated samples show a higher affinity towards R6G as compared to the NH4OH treated samples. This can be assigned to the high number of basic hydroxyl groups due to the reflux in NaOH [47]. This effect is very clear for the Kartini samples whereas for the EISA samples the available surface area also contributes to the large adsorption differences. Therefore, changes in adsorption capacity cannot be assigned to one single parameter since during calcination, the surface area, accessibility, crystal size, crystallinity and other structural characteristic change in a different way depending on the original synthesis applied.

Comparing the influence of the employed stabilization method on the catalytic activity, both EISA and Kartini samples treated with NaOH show low photocatalytic activities as compared to the NH4OH treated samples, irrespective of the thermal treatment. The presence of sodium ions on the surface seems to have a negative effect as the NaOH treated samples show a limited photocatalytic activity (middle grey bars in Fig. 1) compared to the NH4OH treated samples. Indeed, previous studies showed that sodium acts as electron/hole pair recombination center [44]. At increased calcination temperatures, the photocatalytic activity increases.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp. (°C)</th>
<th>Specific surface area (m²/g)</th>
<th>Loss of S_{BET} (%)</th>
<th>Total V_{mic} (ml/g)</th>
<th>Crystal size (nm)</th>
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</thead>
<tbody>
<tr>
<td>EISA nT</td>
<td>C350</td>
<td>271</td>
<td>0.23</td>
<td>NM</td>
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<tr>
<td>C450</td>
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<td>0.18</td>
<td>10</td>
<td></td>
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<tr>
<td>C550</td>
<td>18</td>
<td>93</td>
<td>0.05</td>
<td>23</td>
<td></td>
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<tr>
<td>EISA TNH4OH</td>
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<td>0.26</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>C450</td>
<td>191</td>
<td>22</td>
<td>0.28</td>
<td>7</td>
<td></td>
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<tr>
<td>EISA TNaOH</td>
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<td>127</td>
<td>0.24</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>C450</td>
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<td>307</td>
<td>42</td>
<td>0.42</td>
<td>5</td>
<td></td>
</tr>
<tr>
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<td>0.33</td>
<td>6</td>
<td></td>
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<tr>
<td>Kartini TNaOH</td>
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<tr>
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<td>0.15</td>
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<td>0.31</td>
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<td>153</td>
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<td>0.29</td>
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<td>Cartini TNH4OH</td>
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</tr>
<tr>
<td>C650</td>
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<td>28</td>
<td>0.16</td>
<td>6</td>
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</tr>
</tbody>
</table>

* Specific surface area (S_{BET}) and total pore volume (Tot. V_{mic}) determined by N₂ sorption at ~196 °C.

* Crystal size derived from XRD at 48.14 °C applying the Scherrer equation.
Fig. 1. (A) Results of photocatalytic test using UV-analysis in which 8 mg of catalyst was added to 50 mL \(4 \times 10^{-5}\) M R6G-solution. Adsorption capacity determined after 60 min (EISA TNaOH) and 120 min (EISA TNaOHH) adsorption–desorption equilibrium without UV illumination. After equilibrium, photocatalytic experiments were performed at room temperature during 60 min of UV-illumination. (B) Results of photocatalytic test using UV analysis in which 8 mg of catalyst was added to 50 mL \(4 \times 10^{-5}\) M R6G-solution. Adsorption capacity determined after 60 min (Kartini TNaOH) and 120 min (Kartini TNaOHH) adsorption–desorption equilibrium without UV illumination. After equilibrium, photocatalytic experiments were performed at room temperature during 60 min of UV-illumination. Adsorption, Photobleaching, Total Conversion.

![Graph](image_url)

Fig. 1 (continued)

Although the specific surface area decreases, whatever the synthesis method, the photocatalytic activity of the NH\(_4\)OH post-treated samples increases after calcination at 650 °C (see Fig. 1). This increase is much larger in NH\(_4\)OH stabilized materials as compared to NaOH stabilized materials and seems to coincide with the previously reported differences in crystallinity (EISA TNaOH C450: 68 ± 3%, determined by EELS and EISA TNaOHC450: 40 ± 6%, determined by EELS [39]) and differences in crystal size (Table 1 and XRD in Fig. S1) upon heating. The rather limited increase in photocatalytic activity of the NaOH treated Kartini samples could be correlated to the inhibited crystallization (see Fig. S1) during thermal treatment in combination with the presence of sodium ions. The photocatalytic activity of the NaOH post-treated EISA samples is higher compared to the NaOH-treated Kartini samples, but still very low compared to the other investigated photocatalysts. It is hard to subscribe this observation to one single parameter because the impact of other structural changes cannot be excluded.

Besides UV–Vis measurements, in which the photoinduced bleaching of R6G is studied, total organic carbon-analysis has been performed in order to study the effect of the alkaline post-treatment on the photomineralization to CO\(_2\) in more detail [40]. As shown in Fig. 2, the obtained total organic carbon-results are in correspondence with the UV–Vis measurements and the same trends are observed. For the Kartini samples, enhanced photobleaching and enhanced photomineralization activity can be observed as compared to the EISA samples. This proves that the further degradation of the dye and its intermediates into CO\(_2\) can take place, although the activity towards photomineralization is lower.

In general, it can be concluded that the Kartini samples show a higher thermal stability and photocatalytic activity compared to the EISA samples due to the use of small pre-synthesized crystals. Post-treatment by NaOH is the most efficient way to control the crystal growth during calcination resulting in more stabilized structures irrespective of the preparation method (Kartini/EISA). Even though post-treatment with NaOH results in more stabilized structures, these sodium ions act as recombination center resulting in low photocatalytic activities. From catalytic point of view, the NH\(_4\)OH post-treatment is superior. Although the Kartini samples are characterized by a lower surface area as compared to the EISA samples, there high crystallinity results in higher photomineralization and photobleaching capacities as compared to EISA. However, as stated above, it is clear that also other structural parameters and changes influence the observed differences. It is difficult to distinguish all.

### 3.1.2. Template free mesoporous Ti-based materials

#### 3.1.2.1. Nanotubes

Table 2 presents the surface areas of the thermally treated Na-TNT and H-TNT samples (obtained by ion-exchange of Na-TNT). Here, large differences in initial surface area of Na-TNT and H-TNT are observed. The underlying reason for these differences is still unclear, but it can be partially attributed to the higher molar mass of Na compared to the intercalated protons and the fact that surface area is given as square meters per gram. Furthermore, as described by Qamar et al. [48], it is possible that a higher amount of nitrogen gas (kinetic diameter of 0.364 nm) is adsorbed between the layers of H-TNT (0.62 nm) compared to Na-TNT (0.74 nm), due to the much smaller dimensions of the hydrogen ions. In function of increased temperature, it is clear that the surface area and total pore volume of both

![Graph](image_url)

Fig. 2. Results of photocatalytic test (8 mg of catalyst in 50 mL \(4 \times 10^{-5}\) M R6G-solution): photobleaching (UV–Vis analysis, 60 min) and photomineralization (µV-TOC analysis, 120 min).
Na-TNT and H-TNT seriously decreases around 450 °C (see Table 2). This effect is larger for H-TNT than for Na-TNT. In order to rationalize this decrease, DSC and HR-TEM measurements were performed. The DSC spectra of both Na-TNT and H-TNT, presented in Fig. 3, show a broad peak at 200–300 °C attributed to the loss of structural water and due to condensation of hydroxyl groups. For H-TNT, the exothermic peak between 350 and 420 °C is assigned to recrystallization of trititanate to anatase [25]. No changes occur at this temperature for Na-TNT. HR-TEM shows that calcination of H-TNT at temperatures higher than 350 °C results in the destruction of the nanotube morphology of H-TNT (see Fig. 4A–C) due to recrystallization into anatase particles. The last peak in DSC around 500 °C, originates from the recrystallization of anatase particles into rutile [25]. At the same temperature, the sodium trititanate nanotubes (Na$_2$Ti$_3$O$_7$) start to recrystallize into sodium hexatitanate (Na$_2$Ti$_6$O$_13$) around 450 °C [49,50] (Fig. 4). Furthermore, the morphology of the sodium trititanate nanotubes changes during this recrystallization (Fig. 4D and E) although it is much less drastic as for H-TNT. In general, it is clear that sodium nanotubes are more stable compared to hydrogen nanotubes. The influence of the changes in morphology, crystallinity, crystal size, crystal phase and surface area on the adsorption capacity and photocatalytic activity is shown in Table 2. The adsorption capacity of both H-TNT and Na-TNT decreases at higher calcination temperatures. Although this can be directly correlated to the decreasing surface area, other parameters like the presence of the sodium ions and recrystallization could also influence the adsorption characteristics. Concerning the photocatalytic activity of the different samples, it can be concluded that all Na-TNT samples have a limited activity despite their similar adsorption capacity due to the presence of sodium and its high band gap energy (3.4 eV). In contrast to Na-TNT, the photocatalytic activity of the H-TNT is relatively high and increases in function of elevated calcination temperature (>350 °C). This can be attributed to recrystallization of the structure into highly photoefficient anatase. Although, also other structural changes could take part in the enhanced activity.

So, although sodium nanotubes have a much better thermal stability than hydrogen nanotubes, the presence of sodium ions severely diminishes its catalytic performance as compared to the less stable hydrogen nanotubes. Hydrogen nanotubes recrystallize into more photocatalytic active nanoparticles at temperatures higher than 350 °C. However, this is not very interesting since the catalyst is destroyed and the nanoparticles are hard to recover out of solution.

3.1.2.2. Commercial titanium dioxide (P25 Evonik®). P25 Evonik® is a very fine, commercially available powder (particle size ~20 nm) with low surface area (50–60 m$^2$/g). It has a high photocatalytic activity due to its crystallinity and the balanced ratio anatase/rutile [51]. However, little is known about the thermal stability of the structure and the effect on the photocatalytic activity. In Table 3, it can be seen that the calcination temperature has a minor influence on the surface area (difference of 12 m$^2$/g between P25 nC and P25 C550). In function of increased calcination temperature, a clear decrease in total pore volume can be observed at elevated temperatures, assigned to strong aggregation of the particles during calcination (see SEM picture: Fig. S2). Note that in this case the total pore volume originates from interparticle porosity as P25 is not porous. This results in a lower adsorption capacity.

![Figure 3. DSC of H-TNT nC and Na-TNT nc.](image)

![Figure 4. HR-TEM: (a) H-TNT nc, (b) H-TNT C350, (c) H-TNT C450, (d) Na-TNT nC and (e) Na-TNT C550.](image)
by the enlargement of the pores allowing a much easier diffusion of the R6G molecules and/or by the increased crystallinity [45,52]. Since the adsorption capacity is only 0.1 (10^{-5} M) despite the high specific surface area of Millenium PC500, the adsorption seems to only appear at the external surface (cf. P25). This might explain why differences in inner porosity upon increased temperature, do not result in changes in adsorption capacity. By using pyridine chloride (much smaller dimensions) as artificial pollutant instead of R6G, the importance of the accessibility of the active sites is clearly shown (see Table 3). Due to the loss of available surface area (84%), the adsorption of pyridine chloride drops by 80% whereas no effect was observed for R6G confirming that the R6G can't enter into the majority of the pores of Millenium PC500 nC.

If the photocatalytic activity of the initial and thermally treated titanium dioxide towards R6G is compared at 350 °C, crystallinity and accessibility. Upon increased calcination temperature, the surface area of millionium PC500 decreases whereas the pore sizes and crystallinity [52] increase.

3.2. Mechanical stability

Besides high temperatures, photocatalysts need to be able to withstand pressure (i.e., during storage, formulation, etc.) without losing their specific surface area, morphology and photocata-

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![Table 2](image)

Influence of calcination temperature: (a) results of N$_2$-sorption (surface area (BET) and total pore volume (BJH)); (b) results of photocatalytic test (16 mg of catalyst in 50 ml. 4 × 10^{-5} M R6G-solution) of H-TNT and Na-TNT.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>Loss of $S_{BET}$ (%)</th>
<th>Tot. $V_p$ (mL/g)</th>
<th>Ads.$b$ (10^{-5} M)</th>
<th>Cat.$b$ (10^{-5} M)</th>
<th>Total Conv.$b$ (10^{-5} M)</th>
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<td></td>
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<td>2.16</td>
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<td></td>
</tr>
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<td>1.97</td>
</tr>
<tr>
<td>C550</td>
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<td>48</td>
<td>0.21</td>
<td>1.79</td>
<td>0.16</td>
<td>1.95</td>
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$^a$ Specific surface area ($S_{BET}$) and total pore volume (Tot. $V_p$) determined by N$_2$-sorption at −196 °C.

$^b$ Adsorption (Ads.), catalysis (Cat.) and total conversion (Total Conv.) determined by photocatalytic test.

![Table 3](image)

Influence of calcination temperature: (a) results of N$_2$-sorption (surface area (BET) and total pore volume (BJH)); (b) results of photocatalytic test (16 mg of catalyst in 50 ml. 4 × 10^{-5} M R6G/PyCl); (c) quantification of crystal phases (Rietveld method, XRD) of P25 Evonik® and Millenium PC500®.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>Loss of $S_{BET}$ (%)</th>
<th>Tot. $V_p$ (mL/g)</th>
<th>Ads.$b$ (10^{-5} M)</th>
<th>Cat.$b$ (10^{-5} M)</th>
<th>Total Conv.$b$ (10^{-5} M)</th>
<th>Anatase$^c$ %</th>
<th>Rutile$^c$ %</th>
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<tr>
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<td>3.31</td>
<td>2.63</td>
<td>3.32</td>
<td>83</td>
<td>17</td>
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<tr>
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<td>1.27</td>
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<tr>
<td>C550</td>
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<td>0.78</td>
<td>0.21</td>
<td>1.35</td>
<td>17</td>
<td></td>
</tr>
</tbody>
</table>

NM: not measured.

$^a$ Specific surface area ($S_{BET}$) and total pore volume (Tot. $V_p$) determined by N$_2$-sorption at −196 °C.

$^b$ Adsorption (Ads.), catalysis (Cat.) and total conversion (Total Conv.) determined by photocatalytic test.

$^c$ Percentage crystal phase determined by applying the Rietveld method XRD.

(19% at 550 °C) and a decreased photocatalytic activity (at 550 °C, 24% of its original photocatalytic activity is lost). To clarify the effect of aggregation on the photocatalytic activity, the photocatalytic test was repeated using a pollutant with smaller dimensions (pyridine chloride) compared to R6G. Now, it can be seen that the decrease in photocatalytic activity of P25 after calcination at 650 °C is very limited (6%) compared to R6G (24%). The differences in photocatalytic activity of the thermally treated P25 towards PyCl and R6G clearly shows that the use of a certain catalyst strongly depends on the treatment to which the photocatalysts was subjected to. By using Rietveld quantification (XRD) the effect of the calcination temperature on the ratio anatase/rutile was studied (Table 3). It is clear that temperature has a negligible effect on the crystallinity of P25 as well as on the crystal size of the anatase.

3.1.2.3. Commercial titanium dioxide (Millenium PC500®): Millenium PC500® is a porous, commercially produced titanium dioxide powder. Table 3 shows that the surface area seriously diminishes (84%) in function of increased calcination temperature whereas the decrease in total pore volume is less drastic (41%). After calcination at 350 °C, more than 60% of the initial surface area has already been lost. The corresponding isotherms and pore size distributions (see Fig. 3) show that the smaller pores are disappearing as temperature increases, whereas larger pores and interparticle spaces are being formed, explaining the discrepancy in the decrease in specific surface area and total pore volume. These changes in porosity coincide with a substantial growth in crystal size. Despite drastic structural changes during thermal treatment, the adsorption capacity towards R6G isn’t influenced. This could be caused
lytic activity. Therefore, the mechanical stability of the as-synthesized materials is tested by pelletizing the samples at 296 and 740 MPa.

3.2.1. Templated Ti-based materials synthesized via the Kartini and EISA method

As discussed in previous section, the surfactant, present in the alkaline post-treated EISA and Kartini samples, can be completely removed at 450 °C. Therefore, all the samples were calcined at 450 °C in order to avoid additional stabilization coming from small amounts of surfactant left in the pores.

Considering the surface area of both EISA and Kartini samples after pressurizing (Table 4), it is clear that EISA NaOH has a lower mechanical stability as compared to EISA NH4OH and both Kartini samples. This can be clearly seen from the increased loss in surface area after applying a pressure of 740 MPa, since the NaOH and NH4OH post-treatment of the samples did not alter significantly since the loss of surface area is very limited for these samples. The pores seem still well accessible despite the presence of local pore narrowing.

3.2.2. Template free mesoporous photocatalysts

3.2.2.1. Nanotubes. Table 5 and Fig. S7 show the N2-sorption results (BET) and total pore volume (BJH) determined by N2-sorption at –196 °C. Changes in pore diameter appear upon increasing pressure, resulting in materials with partially and locally narrowed pores at 740 MPa (two-step desorption) [53]. This might influence the photocatalytic activity and adsorption capacity of the samples. Table 4 shows that the adsorption capacity and photocatalytic activity of EISA TNaOH C450 decreases as a function of increased pressure. This is in agreement with the drop of available surface area of EISA TNaOH in function of increased pressure. Moreover, the accessibility of the active sites within the pores diminishes due to pore narrowing (Fig. S6A). Even if smaller pollutant molecules (pyridine chloride) are applied (Table 4), decreased adsorption capacities can be observed in function of pressure. The adsorption capacity and photocatalytic activity of all other samples does not alter significantly since the loss of surface area is very limited for these samples. The pores seem still well accessible despite the presence of local pore narrowing.
multiwalled structure (Fig. 5C). The sodium nanotubes have therefore a higher mechanical stability of the morphology of the tubes compared to the hydrogen nanotubes. The reason for this might be the better interaction of the sodium with the surrounding negative loaded Ti-O layers compared to the intercalated protons [54].

The loss of the nanotube morphology of H-TNT and the limited accessibility of the active sites due to the large decrease in interparticle porosity, results in a tremendous decrease in photocatalytic activity and adsorption capacity (Table 5). Even though the Na-TNT have a larger decrease in surface area and total pore volume, their original photocatalytic activity is very low, which makes them not very interesting as photocatalysts.

3.2.2.3. Commercial titanium dioxide (P25 Evonik®). In Table 6, the influence of pressure on the surface area and total pore volume of P25 Evonik® is presented. Although, non-porous P25 Evonik® becomes more dense in function of pressure as shown in Fig. 6, there seems to be no loss of external surface area under the applied pressure. Nevertheless, considering the results of the photocatalytic test (Table 6), a clear influence of the increased pressure on the adsorption capacity and photocatalytic activity can be observed. Indeed, the adsorption capacity decreases by 50% and the photocatalytic activity decreases with 65% after applying a pressure of 740 MPa. Similar results are obtained if a smaller artificial pollutant like PyCl is applied. Therefore, it can be concluded that P25 Evonik® loses its high photocatalytic activity after pressurizing. Even though nitrogen has still access to the total specific surface area after pressurizing, the pollutants seem to suffer from a limited accessibility of the active sites (for both R6G and PyCl). Again, it is clear that the suitability of the catalyst under the applied conditions depends on the size of the pollutant.

3.2.2. Commercial titanium dioxide (Millenium PC500®). Although Millenium PC500® is a highly porous photocatalyst, the adsorption of R6G is relatively small (see Table 6). This can be related to the limited accessibility of the pores by R6G as described in previous

<table>
<thead>
<tr>
<th>Pressure (MPa)</th>
<th>( S_{\text{BET}} , (\text{m}^2/\text{g}) )</th>
<th>Loss of ( S_{\text{BET}} , (%) )</th>
<th>Tot. ( V_p , (\text{mL/g}) )</th>
<th>Ads. ( (10^{-5} , \text{M}) ) R6G</th>
<th>Cat. ( (10^{-5} , \text{M}) ) R6G</th>
<th>Total Conv. ( (10^{-5} , \text{M}) ) R6G</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>0</td>
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<td>0.16</td>
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</tr>
<tr>
<td>296</td>
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<td>1.15</td>
</tr>
<tr>
<td>Millenium PC500</td>
<td>0</td>
<td>364</td>
<td>0.25</td>
<td>0.05</td>
<td>0.22</td>
<td>0.71</td>
</tr>
</tbody>
</table>

a Specific surface area \( (S_{\text{BET}}) \) and total pore volume \( (Tot. \, V_P) \) determined by N2-sorption at \(-196 \, ^\circ\text{C}\).
b Adsorption (Ads.), catalysis (cat.) and total conversion (Total Conv.) determined by photocatalytic test.
section (Millenium PC500® is characterized by very small pores, see Fig. S8). If a pressure of 296 MPa is applied, the total pore volume decreases by 32% and the available surface area decreases by 35%. This results in a severely diminished adsorption capacity and photocatalytic activity. At a mechanical pressure of 740 MPa, 39% of the initial surface area and 41% of the total pore volume is lost resulting in a decreased adsorption capacity (58%) and the photocatalytic activity (75%). Nevertheless, if pyridine chloride is used as artificial pollutant, the adsorption capacity decreases with only 11% and the photocatalytic activity with 36% after a pressure of 740 MPa suggesting the easier accessibility of pyridine chloride compared to R6G. In general, it is clear that structure suffers severely from mechanical stress.

If the mechanical stability of the commercial titania catalysts and the as-prepared photocatalysts is compared, it is clear that the porous post-treated Kortini and EISA samples have superior properties over the hydrogen nanotubes and the commercial powders. For the hydrogen nanotubes and Millenium PC500®, a clear structural collapse can be observed at increased pressures. Although, this can't be observed for P25 Evonik® (since it is non-porous), both P25 and Millenium PC500 seem to suffer from a diminished accessibility of the active sites after pressure has been applied, resulting in a reduced photocatalytic activity.

4. Conclusion

In this study, the thermal and mechanical properties of eight different as-prepared and commercially available photocatalysts were studied. It is shown that the changes in calcination temperature/mechanical stress have a large impact on different characteristics of the material. Besides changes in available surface area and pore size, the morphology of the samples as well as the crystal size, particle size distribution, mass transport, crystallinity and crystal phase can be altered. Therefore, the observed changes in adsorption capacities and photocatalytic activities cannot be assigned to one single phenomenon. This makes it hard to predict the stability of the adsorption capacity and photocatalytic activity of the photocatalyst with respect to thermal and mechanical stress. In this respect, it shows the need to define a general/standard method to compare different photocatalysts as was exemplified here. Furthermore, it is shown that the photocatalytic properties do not necessarily deteriorate under thermal stress, but can be improved due to crystallization, even though the initial material is (partially) destroyed. Therefore, the usefulness of a specific type of photocatalyst strongly depends on the application and the temperature/mechanical stress to which it needs to resist.

In general, it is clear that the NaOH post-treatment is beneficial for the mechanical and thermal stabilization of mesoporous titania. However, it has a negative effect on the photocatalytic activity. Other bases are therefore to be preferred. Hydrogen nanotubes are characterized by low mechanical and thermal stability as the nanotube morphology can be completely destroyed at increased temperature or mechanical stress as low as 296 MPa. Sodium nanotubes are more stable, but show low photocatalytic activities. Although, P25 Evonik® is recognized as a highly efficient photocatalyst, its activity can be seriously reduced by thermal or mechanical stress, which seems originate from the reduced accessibility of the active sites.

Acknowledgements

Prof. B. Van Der Veken is gratefully acknowledged for the DSC measurements. Joke Van Laer and Matthias Laleman (Shimadzu) are acknowledged for their technical support with respect to the development of the μ TOC. This work has been performed in the frame of the PWO project (G. 0237.09) and the GOA-project (41/FA070200/799).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.micromeso.2012.01.036.

References


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