



Synthesis and application of layered titanates in the photocatalytic degradation of phenol



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ABSTRACT

This study proposes a direct synthetic route to single titanate sheets through the mild and versatile conditions of the “chimie douce”. The stages of the production include the complexation of the titanium alkoxide precursor by benzoic acid, the formation of titanium oxo-clusters and their controlled transformation into single sheet titanates during the hydrolysis stage. The resulted material appears to be an excellent precursor for self-organized TiO₂ nanotubes formation which presents an excellent activity as photocatalyst in the photo-degradation of phenol.

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1. Introduction

Over the past decades, the TiO₂ derived nanosized materials have been widely investigated for vast applications, including gas sensors, photocatalysts, solar cells and biomedical applications [1–5]. More precisely, the TiO₂ based nanotubes (TNT) have been extensively studied since their peculiar properties, like high specific area, ion-exchange ability and photocatalytic activity [6]. Currently developed methods for TNT production include the assisted-template method [7,8], the electrochemical anodic oxidation [9,10] and hydrothermal treatment [11–14]. However, all these methods suffer some drawbacks, like complicated fabrication process in the case of template method, limitation of mass production and high fabrication costs for the electrochemical method and long reaction duration and difficulties in achieving the uniform size nanotubes through the hydrothermal treatment. Nowadays, the most popular method remains the hydrothermal treatment of TiO₂ anatase in NaOH solutions, firstly reported by Kasuga et al. [11].

The layered titanates have recently received a great attention due to their interesting interlayer chemistry, high ability to ion exchange/intercalation reactions and potential applications in the synthesis of new nanomaterials. Moreover, they can undergo exfoliation/delamination upon intercalation of the bulky

organic molecules, producing single sheets with distinctive 2D morphology, which are very attractive building blocks for producing artificial architectures, hybrid multilayers or microporous materials [15].

The only known method for the synthesis of layered titanates is the solid–solid reaction at high temperature between TiO₂ and an alkali metal carbonate, followed by acid exchange reaction to produce the protonated form H_xTi_{2–x/4}□_{x/4}O₄·H₂O [16,17].

On the other hand, heterogeneous photocatalysis has found increasing interest as a promising technique for water and air remediation being an environmental friendly and sustainable technology [18]. So far, TiO₂ in its form anatase or anatase–rutile mixtures has been the most widely studied material to be used as photocatalyst. However, this material still presents some drawbacks, such as the high degree of recombination of photogenerated charges which limit the efficiency of the photocatalytic processes. Thus, one interesting challenge nowadays is the design and development of tailored nanostructured materials to overcome these limitations. In this context, TiO₂ nanotubes due to their 1D geometry may allow a faster and shorter charge transport to the surface which would lead to less recombination rate and consequently to the improving in the overall efficiency of the material [19].

This study proposes a direct synthetic route to exfoliated layered titanates and their conversion into self-organized TiO₂ nanotubes either by a simple contact with sodium hydroxide solution or by a hydrothermal synthesis. The photocatalytic activity of the produced materials is tested by following the photocatalytic degradation of phenol, chosen as model reaction.

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2. Experimental

2.1. Modified sol–gel synthesis

In a typical synthesis, 1 mol of titanium (IV) butoxide (Sigma–Aldrich ASC 97%), and 4 mol of benzoic acid (Sigma–Aldrich ASC 99.5%), were added to 5 mol of absolute ethanol (Prolabo, 100%) and stirred under heating up to 92 °C until the homogenization of the solution. After that, 8 mol of distilled water for the hydrolysis step was added dropwise and maintain under vigorous stirring for 3 h. The obtained slurry was dried overnight at 80 °C. The excess of organic compounds was removed from the resulting solid by Soxlet extraction during 24 h using ethanol as solvent. The final product was then dried at room temperature. The sample will be labelled as LT.

A portion of the resulting solids was immersed in a 0.1 mol L⁻¹ HCl solution for 24 h in order to assure the protonic exchange, washed abundantly with distilled water to neutral pH and finally dried at room temperature. The sample is labelled as H-LT.

2.2. Ti-nanotubes synthesis

The product, obtained after the modified so–gel method (LT), was dispersed in an aqueous solution of NaOH (7 mol L⁻¹) and stirred for 24 h, washed with distilled water and dried at 80 °C. The as prepared sample is called Na-TNT (S).

In a similar way, suspension of the same sol gel product (LT) and 7 mol L⁻¹ NaOH was submitted to autogeneous pressure at 130 °C for 24 h, and after, washed with distilled water and dried at 80 °C. The as prepared sample is called Na-TNT (HT).

Finally Na-TNT(S) and Na-TNT(HT) solids were immersed in a 0.1 mol L⁻¹ HCl solution for 24 h, washed abundantly to neutral pH and finally dried at room temperature. The samples produced are labelled respectively H-TNT (S) and H-TNT (HT).

2.3. Characterizations

X-ray diffraction (XRD) analysis was performed on an X'Pert Pro PANalytical. Diffraction patterns were recorded with Cu K α radiation (40 mA, 45 kV) over a 2 θ -range of 3–60° and a position-sensitive detector using a step size of 0.05° and a step time of 80 s.

X-ray diffraction (XRD) analysis at high temperature was performed in a high temperature camera Anton Paar HTK 1200 coupled with an X'Pert Pro Philips diffractometer, equipped with X'Celerator detector with an opening of 2.18°, a step of 0.05° and an equivalent time acquisition of 30 s. The diffractograms were taken every 50 °C in the 50–60° C temperature range, over a 2 θ -range of 3–60° in flow of synthetic air.

The Raman spectra were recorded on a dispersive Horiba Jobin Yvon LabRam HR800 microscope with a 20 mW He-Ne green laser (532.1 nm), without filter and with a 600 g mm⁻¹ grating. The microscope used a 50 \times objective with a confocal pinhole of 1000 μ m.

BET surface area and porosity measurements were carried out by N₂ adsorption at 77 K using a Micromeritics ASAP 2010 instrument.

Transmission electron microscopy (TEM) observations were carried out in a Hitachi H 800 microscope operating at 200 kV. The samples were dispersed in ethanol by sonication and dropped on a copper grid coated with a carbon film.

2.4. Photocatalytic experiments

The evaluation of the photocatalytic activity was performed by using the photooxidation of phenol as model reaction.

Suspensions of the samples (1 g L⁻¹) in phenol solution (25 ppm) were placed in a 200 ml pyrex discontinuous batch reactor

Table 1

Specific surface area and pore volume for the studied samples.

Sample	BET specific surface area, m ² g ⁻¹	Pore volume, cm ³ g ⁻¹
LT	75	0.0576
H-LT	163	0.1089
Na-TNT (S)	66	0.0620
H-TNT (S)	241	0.1769
Na-TNT (HT)	67	0.0673
H-TNT (HT)	173	0.1487

enveloped by an aluminum foil and illuminated through a UV-transparent Plexiglas® top window (threshold absorption at 250 nm) by an Osram Ultra-Vitalux lamp (300 W) with sun-like radiation spectrum and a main line in the UVA range at 365 nm. The intensity of the incident UVA light on the solution was determined with a PMA 2200 UVA photometer (Solar Light Co.) being ca. 140 W m⁻².

Magnetic stirring and a constant oxygen flow as oxidative agent were used to produce a homogeneous suspension of the catalyst in the solution. Prior illumination, catalyst-substrate equilibration was ensured by stirring the suspension 20 min in the dark. Phenol concentration was followed by HPLC technique (Agilent Technologies 1200) equipped with UV-Vis detector using Eclipse XDB-C18 column (5 μ m, 4.6 \times 150 mm). Mobile phase was water/methanol (65:35) at a flow rate of 0.8 ml min⁻¹.

Blank experiments were performed in the dark as well as with illumination and no catalyst, without observable change in the initial concentration of phenol in both cases.

3. Results and discussion

Before starting the discussion of the results, one precision should be made. In general, the subsequent treatment of all the samples by acid solutions does not provoke any changes in morphology, shape and/or crystallinity. That is why only the characterization of the protonated forms is presented through the whole manuscript. The only difference results in the specific surface area and pore volume as presented in Table 1.

The results of the specific surface area measurements show that the treatment of the sol–gel product sample (LT) with sodium hydroxide solution does not change excessively the initial surface area. However, the subsequent acid treatment and more precisely the abundant washing till neutral pH provoke a significant increase of the surface area caused by pore liberation. Nevertheless the applied Soxlet extraction in ethanol of the organic phase, the presence of Na-benzoates and/or benzoic acid rests could be imagined as responsible for pore filling into the non-acid treated samples. The contact with acid solutions produces mesoporous materials with rather high specific surface area neighbouring 200 m² g⁻¹.

The XRD pattern of the synthesized protonated sol-gel product (H-LT) is presented in Fig. 1.

The obtained reflections indicate the production of lamellar structure which can be indexed as (0 k 0) body centered orthorhombic titanate lepidocrocite like structure. In addition, the asymmetric line shape with a tail toward higher angle diffractions, in the 0 1 0 reflection peak, was reported by Sasaki et al. [20] as typical of a two-dimensional lattice, pointing to the production of 2D network of the layered titanates.

A more detailed study of the H-LT pattern indicates the presence of an amorphous phase, which could be interpreted either as a combination of scattering between water and/or organic molecules (benzoates) in between the titanate sheets or by the presence of low crystalline titania anatase phase which major diffraction appears at 2 θ ~ 25 (indicated with the cross symbol in Fig. 1). Furthermore, the diffraction lines at around 2 θ ~ 8 and 17° (triangles) specified also the presence of an additional phase identified as crystalline

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