



Mesoporous titania with anatase walls by flash induction calcination



Karine Assaker^a, Taissire Benamor^{b,1}, Laure Michelin^b, Bénédicte Lebeau^{b,*}, Claire Marichal^b, Marie-José Stébé^a, Jean-Luc Blin^{a,*}

^a Université de Lorraine/CNRS, SRSMC, UMR 7565, F-54506 Vandoeuvre-lès-Nancy cedex, France

^b Université de Haute Alsace (UHA)/CNRS, Equipe Matériaux à Porosité Contrôlée (MPC), Institut de Science des Matériaux de Mulhouse (IS2M), UMR 7361, F-68093 Mulhouse cedex, France

ARTICLE INFO

Article history:

Received 12 June 2014

Received in revised form 4 September 2014

Accepted 9 September 2014

Available online 18 September 2014

Keywords:

Ordered mesoporous TiO₂

Flash induction

Mesoporosity release

Crystallization

Anatase

ABSTRACT

Induction heating has been used to thermally treat mesostructured TiO₂ with hexagonal 2D structure prepared by a combined Liquid Crystalline Template (LCT) and Evaporation Induced Self-Assembly (EISA) synthesis method. Induction treatment induces the decomposition of the structuring agent P123 and the formation of anatase. Highly ordered mesoporous titania with a semi crystalline framework can be obtained very fast, i.e. 5 min at 460 °C or 15 min at 300 °C. The recovered materials have similar structural, textural properties and photoactivity towards the decomposition of methyl orange than the mesostructured TiO₂ obtained after ethanol extraction followed by a calcination at 400 °C in a conventional furnace.

© 2014 Elsevier Inc. All rights reserved.

1. Introduction

Titanium dioxide represents a good photocatalyst for wastewater treatment, air purification or self-cleaning surfaces and mesoporous titania with controlled porosity which usually allow to reach high surface area are of interest for these applications [1,2]. However, on the contrary of ordered mesoporous silica, their synthesis is much more difficult. Two mechanisms can lead to the formation of these ordered TiO₂ mesostructures [3–5]. The first one is the soft templating pathway which implies the co-assembly of the titania precursor and surfactant, similar to the preparation of ordered mesoporous silica. To release the porosity, the surfactant has to be removed and to do so. Different strategies have been developed such as calcination, solvent extraction, chemical oxidation, and supercritical fluid extraction, etc. [6–13]. However, the surfactant removal usually leads to the collapse of the mesostructure [14]. This collapse is mainly due to the phase transition from amorphous titania to anatase at about 250 °C and to rutile at 600 °C. The second way to prepare

ordered mesostructures is the hard-templating method. In that case the mesoporous titania is prepared in a confined space, for example via replication of mesoporous silica. Since the template prevents collapse of the mesostructure upon calcination, the main advantage of this method is the preservation of the ordered mesopore channel array during the crystallization step at high temperature. Recently, a synthesis route based on Evaporation Induced Self-Assembly (EISA) coupled with Liquid-Crystal Templated (LCT) methods was recently developed in Blin's research group to produce ordered mesoporous titania with high surface area and good thermal stability [15]. Mesostructured titania were thermally treated from 150 °C to 550 °C under conventional calcination conditions (2 h under air in muffle furnace). Such calcination procedure is a long time process and thus energy consuming. Recently a flash calcination process using induction furnace was reported by Lebeau's research group to remove the P123 Pluronic organic template from ordered SBA-15 type mesostructured silica [11]. The total P123 decomposition was achieved after 15 min of induction thermal treatment at 300 °C (or 5 min at higher temperatures). In the present paper we report the study of the thermal decomposition by induction of the P123 organic template occluded within porosity of mesostructured titania. In particular the structural and textural characteristics of mesostructured titania material were carefully investigated and compared to homologous materials heat treated under conventional conditions [15].

* Corresponding authors.

E-mail addresses: benedicte.lebeau@uha.fr (B. Lebeau), jean-luc.blin@univ-lorraine.fr (J.-L. Blin).

¹ Current address: Centre de Recherche et Technologie des Eaux (CERTe), Soliman 8020, Tunisia.

2. Experimental section

2.1. Materials preparation

Mesostructured titania were prepared with by a combined Liquid–Crystal Templating (LCT)–Evaporation Induced Self Assembly (EISA) method according a procedure previously reported [15,16]. Typically, 1 g of triblock copolymer P123 (EO)₂₀(PO)₇₀(EO)₂₀ (Aldrich) was dissolved in 20 g of ethanol (99% Aldrich) under stirring at room temperature. Then 2 g of a hydrochloric acid (ACS reagent, 37%, Sigma–Aldrich) solution, 3 g of titanium isopropoxide (TiOpr) (97% Aldrich) and 2 g of water were added. After addition of TiOpr, the mixture was directly evaporated under vacuum to remove ethanol and isopropanol released by the hydrolysis of TiOpr. Samples were dried in an oven at 40 °C for 12 h. Then, they were placed under atmosphere of NH₃ during 12 h to allow the precipitation of TiO₂. The obtained mesostructured titania materials have amorphous walls.

To remove the P123 and liberate the porosity of the amorphous mesostructured titania, the as-synthesized samples were subjected to calcination at different temperatures and durations in an induction furnace (Bead preparation system for X-ray fluorescence named Minifuse 2 from Philips instruments). The power of the induction furnace was varied between 15 and 70 W which corresponds to temperatures that were measured with a thermocouple between 300 °C and 600 °C, respectively. For this purpose, 100 mg of as-synthesized samples were spread in a platinum crucible and calcination was performed at 300 °C (for 15, 15 + 15, 15 + 30 and 30 + 30 min), 460 and 600 °C (for 5 and 15 min). The heating rate of the induction calcination is very fast: ~3 °C/s for 300 °C and ~6 °C/s for 600 °C. The samples are designated as follow: *I–T–t* with *I* for induction furnace calcined samples, *T* (°C) and *t* (min) are temperature and duration of calcination, respectively.

For comparison a mesostructured TiO₂ was also calcined by using a conventional calcination method, about 250 mg of the sample obtained after P123 extraction by ethanol during 8 h were spread in a porcelain crucible and put in the muffle furnace. The temperature was raised to 400 °C with an average heating rate of about 1 °C/min under N₂, and then holding at the same temperature for 2 h under O₂. The resulting sample is designated by C-400.

2.2. Characterization techniques

SAXS measurements were carried out using SAXSess mc2 (Anton Paar) apparatus. It is attached to a ID 3003 laboratory X-ray generator (General Electric), equipped with a sealed X-ray tube (PANalytical, $\lambda_{\text{Cu}}(K\alpha) = 0.1542$ nm) operating at 40 kV and 50 mA. A multilayer mirror and a block collimator provide a monochromatic primary beam. A translucent beam stop allows the measurement of an attenuated primary beam at $q = 0$. Mesoporous materials are introduced into a powder cell before being placed inside an evacuated chamber equipped with a temperature controlled sample holder unit. Acquisition times are typically in the range of 1–5 min. Scattering of X-ray beam is recorded by a CCD detector (Princeton Instruments, 2084 × 2084 pixels array with 24 × 24 μm^2 pixel size) placed at 309 mm from the sample holder in the q range from 0.09 to 5 nm⁻¹. Scattering data, obtained with a slit collimation, contain instrumental smearing. Therefore, the beam profile has been determined and used for the desmearing of the scattering data. All data were corrected for the background scattering from the empty cells.

Powder X-ray diffraction patterns were recorded using a PANalytical X'Pert PRO diffractometer equipped with a Cu X-ray tube ($\lambda_{\text{Cu}}(K\alpha) = 1.5418$ nm) operating at 45 kV and 40 mA and an X'Celerator detector. Fixed divergence slit (1/16), mask (10 mm) and antiscatter slit (1/8) were used at primary beam for the current

analysis. As we have small quantities of product, they were deposited on a glass support. For the quantification of the anatase, programmable divergence slit and mask (10 mm) were used in order to maximize the intensity of the peaks and decrease the analysis time. All the samples were compacted on 16 mm diameter support. After subtraction of the background, the area of the peak at $48^\circ 2\theta$ was calculated. This peak was chosen because it is the first most intense and isolated peak which is not in the range of the amorphous TiO₂ signal. A calibration curve with physical mixture of anatase 10 nm (purchased from Alfa Aesar) and amorphous TiO₂ (prepared according a modified procedure reported in [17]: in our case the precipitation of TiOpr occurs at 40 °C and the drying of the gel is performed at room temperature) was realized. The results obtained by the calibration curve were checked by the method of standard addition with anatase 10 nm in one of the mesoporous TiO₂ sample to analyze. The difference between the two methods was less than 5%.

Transmission Electron Microscopy (TEM) images of the samples were acquired using a Philips CM200 microscope working at 200 kV. Prior to the observation, the powder was dispersed into chloroform with ultrasounds and a few drops of the suspension were deposited at the surface of a copper observation grid covered with a formvar/amorphous carbon film. The organization and the porosity of the materials were observed using the bright-field mode, while the localization of the anatase nanoparticles was done in dark-field mode.

N₂ adsorption/desorption isotherms were recorded on a Micromeritics TRISTAR 3000 sorptometer at –196 °C. Samples were previously degassed at 150 °C under low pressure (<0.3 mm Hg) for 12 h.

Raman scattering spectra were collected on a Jobin–Yvon T64000 spectrometer equipped with an optical microscope in confocal mode. The excitation beam (514.5 nm) was focused using a long-frontal 80× objective (numerical aperture 0.85) on an area of about 3 μm^2 . The laser power on the sample was approximately 10 mW. The spectral resolution was 3 cm⁻¹, with a wavenumber precision better than 1 cm⁻¹.

¹H–¹³C solid state CPMAS NMR experiments were performed on a Bruker Avance II-400 spectrometer operating at a Larmor frequency of 100.63 MHz. The spectra were recorded with a $\pi/2$ ¹H pulse duration of 4.5 μs , a contact time of 1.5 ms, a recycle delay of 8 s and spinning frequency of 12 kHz. ¹³C chemical shifts were referenced to tetramethylsilane (TMS). CHN analyses were realized on an Analyzer CHNS/O Thermo Electron Flash EA 1112 Series by Welience, Pôle Chimie Moléculaire, University of Bourgogne, France.

2.3. Photocatalytic activity

Methyl orange (Aldrich) was chosen as organic compound to evaluate the photocatalytic properties of the mesoporous TiO₂ after heat treatments in induction furnace or conventional muffle furnace. Analyses have been performed according to the procedure previously reported [18]. In this previous work, we have tested the reproducibility of the system; several experiments have been performed under the same experimental conditions. The results have shown that the error between three measurements made the same day is usually less than 5% and is mainly due to light intensity drift. When the experiment was repeated days later, the data did not quantitatively differ from the first result and the trends were similar. Every experiment was repeated at least three times, and data were considered acceptable only if for three repetitions, the data for each time point differ by less than 5%.

In a typical experiment 50 mg of calcined TiO₂ have been added to 100 mL of a methyl orange aqueous solution (16 mg per mL). The reaction was carried out with continuous stirring in a quartz

Download English Version:

<https://daneshyari.com/en/article/72771>

Download Persian Version:

<https://daneshyari.com/article/72771>

[Daneshyari.com](https://daneshyari.com)