Microporous and Mesoporous Materials 154 (2012) 187–195

Contents lists available at SciVerse ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

A facile synthesis of well-defined titania nanocrystallites: Study on their growth, morphology and surface properties

Lenka Matějová [a,*], Zdeněk Matěj [b], Olga Šolcová [a]

[a] Institute of Chemical Process Fundamentals of the ASCR, v. v. i., Department of Catalysis and Reaction Engineering, Rozvojová 135, 165 02 Prague 6, Czech Republic
[b] Charles University in Prague, Faculty of Mathematics and Physics, Department of Condensed Matter Physics, Ke Karlovu 5, 121 16 Prague 2, Czech Republic

ARTICLE INFO

Article history:
Received 16 June 2011
Received in revised form 6 October 2011
Accepted 28 November 2011
Available online 6 December 2011

Keywords:
TiO_2 anatase
Nanocrystalline structure
Metal alkoxide
X-ray diffraction
Whole powder pattern modeling (WPPM)

ABSTRACT

The fast and simple synthesis of anatase nanocrystallites by the low-temperature hydrolysis of titanium (IV) alkoxides in the hydrogen peroxide solution followed by calcination of the amorphous titania peroxo-product at temperature in the range 300–450 °C was designed and studied. The phase composition and crystallite-size were evaluated from X-ray diffraction data by the advanced whole powder pattern modeling method together with the crystallite-size distribution and microstructure parameters such as the defect density. Besides that, the textural and surface properties, skeletal density, particle morphology and the purity of nanopowders were determined by nitrogen physisorption, helium pycnometry, mercury porosimetry, XPS, FESEM and the organic elementary analysis. The pure anatase nanocrystallites with the uniform globular structure and the narrow crystallite-size distributions were prepared at the significantly lower temperature (300 °C) in comparison with the conventional chemical methods. The size and shape of anatase crystallites were tailored by the calcination temperature and the type of titanium (IV) alkoxide. Titania nanocrystallites with the excellent uniformity were produced from titanium (IV) *n*-butoxide-type precursor. Correlation between the crystallite growth and the porous structure was observed up to temperature about 400 °C. Above this temperature the crystallite size monotonically increases, whereas the specific surface area is reduced steeply.

© 2011 Elsevier Inc. All rights reserved.

1. Introduction

A large part of the modern material research is focused on the synthesis of porous metal oxides (TiO_2, ZrO_2, SnO_2, CeO_2, ZrO_2–CeO_2, TiO_2–ZrO_2, Al_2O_3–CeO_2, TiO_2–CeO_2, etc.) thanks to their helpful application in many research areas; ecological liquidation (oxidation caused by the UV light effect) of organic contaminants in waste water and air [1–4], dye-sensitized photo electrochemical cells [5], electro chromic devices [6–8], sensors [9], efficient supports of metal species in catalysts for VOCs [10,11] and CVOCs oxidation [12,13], etc. Applications of these porous metal oxides are based on their powdered form as well as on nanolayers deposited on various substrates like glass, silicon, metallic foils, etc. In general, various functionality and catalytic efficiency of these metal oxides are strongly affected by the differences in their textural properties (*e.g.* specific surface area, micropore volume, micro- and mesopore-size), structural properties (*e.g.* crystalline phase composition and/or crystallite size) [14], surface acidity, etc. Therefore, the precise and correct characterization of material properties is also highly requested.

Titania (TiO_2), a member of the above mentioned group, is still under keen photo-catalytic research and many advanced preparation procedures/techniques improving its properties and catalytic performance have been developed and investigated; hydrothermal crystallization [15,16], sol–gel and templated sol–gel [17,18] in combination with super/subcritical drying [19], chemical vapor deposition [20], etc. Usually the synthesis of TiO_2 crystalline phases requires the hard experimental conditions – high temperature (at least above 400 °C), high pressure (in SFE technique the required pressure is above 7.3 MPa) or some special media/atmosphere (*e.g.* plasma/vacuum). Only a few preparation routes of the pure TiO_2 synthesized at mild conditions have been described in literature.

Owing to the higher purity of final TiO_2 [21,22] the titanium (IV) alkoxides (in spite of their reactivity in moisture) are generally preferred as metal precursors instead of titanium chlorides. Wang et al. [23] studied the hydrolysis of titanium (IV) *n*-butoxide in H_2O_2 solution at near room temperature and they proved preparation of the anatase and rutile crystalline phase mixture by thermal treatment of the prepared poly-peroxotitanic complex above 150 °C in the air flow. The transformation of anatase to rutile started at significantly lower temperature (∼150 °C) in comparison with the other conventional methods, where the transformation usually occurs in the temperature range 500–600 °C. Moreover,

---

* Corresponding author. Tel.: +420 220 390 302; fax: +420 220 920 661.
E-mail address: matejova@icpf.cas.cz (L. Matějová).

1387-1811/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2011.11.054

Ti–O–O bonds were confirmed by FTIR analysis in titania samples up to 250 °C. Uekawa et al. [24] prepared pure TiO_2 anatase with crystallite sizes from 9 nm to 15 nm in dependence on the boiling time (from 6 to 48 h) at 75 °C. For preparation the diluted solution made of alkoxide and hydrogen peroxide in ethanol was used. The prepared TiO_2 anatase exhibited the BET surface area between 250 and 440 m^2/g without subsequent calcination. Nevertheless, it possessed mainly microporous character.

This study is focused on the preparation of TiO_2 anatase by the hydrolysis of the titanium (IV) alkoxides in solution of hydrogen peroxide and on a thorough characterization with special attention on the complex preparation process of the pure TiO_2 anatase nanocrystals with respect to the individual steps. A great attention is aimed at the precise and correct chemical and structural characterization of synthesized TiO_2. The possible tailoring of the size and shape of anatase nanocrystallites by combination of the calcination temperature and the type of used titanium (IV) alkoxide is examined. Based on knowledge of peroxo bonds presented in titania samples up to 250 °C [23], the influence of calcination temperature was evaluated above this range. Besides the influence of the used metal precursor type the various calcination conditions; (i) temperature range (300–450 °C) and (ii) duration of thermal treatment (4–10 h), on textural and structural properties – mainly the crystallite growth and the phase composition – was investigated by an up-to-date whole powder XRD pattern modeling method (WPPM) [25]. This method was developed by Scardi and Leoni [26] in 2001 and it is based on a Rietveld-like fitting of the whole XRD pattern with special care of modeling width and shape of diffraction peaks. The WPPM overcomes [27] some approximations and drawbacks involved in the classical approaches as *e.g.* the Scherrer formula and thus it can more reliably reveal the finer details of the real sample microstructure such as the crystallite size distribution [28] or the defect density [29–31].

2. Material and methods

2.1. Preparation

Following chemicals were used for the synthesis: Titanium (IV) isopropoxide ($Ti(OCH(CH_3)_2)_4$) and Titanium (IV) *n*-butoxide ($Ti(O(CH_2)_3CH_3)_4$) (Aldrich, purity > 98 + %), hydrogen peroxide (30% nonstabilized p.a., Lach-Ner) and distilled water.

In a typical synthesis 20 ml of Titanium (IV) *n*-butoxide was added drop by drop to ice-cooled 50 ml 4.4 M H_2O_2 water solution at continuous agitation. The bath temperature was maintained at −1 °C, temperature of the mixture was kept constant at 1–2 °C during the whole experiment. During 45 min mixing the formation of the orange-colored $Ti{\cdot}H_2O_2$ complex was observed together with the oxygen evolution (visible huge amount of bubbles in solution), water and alcohol. The experiment was finished after the formation of the oxygen bubbles nearly stopped. The precipitate was left on air for 24 h to release the rest of oxygen. Then the precipitate was dried in an oven at 150 °C for 5 h. During drying the orange precipitate converted into the yellow precipitate. After drying the precipitate was calcined above 300 °C for the defined time with the heating rate 1 °C/min in a muffle furnace in the air flow to guarantee the decomposition of Ti–O–O– bonds and alcohol. The sample nomenclature is explained in Table 1; footnote a.

2.2. Characterization of TiO_2 powders

The specific surface area, the micropore volume, the total pore volume, the mesopore surface area and the micro- and mesopore-size distribution were evaluated by the nitrogen physisorption at −196 °C performed on an automated volumetric apparatus ASAP2020 Micromeritics (USA). The application of nitrogen and helium with high purity (99.9995%) guaranteed the precision of measured data. Before analysis samples were degassed for 24 h at 105 °C under vacuum (~1 Pa).

The true (helium) and apparent (mercury) density of prepared powders together with the meso- and macropore-size distribution were determined with the use of helium pycnometer (AccuPyc1330, Micromeritics, USA) and high-pressure mercury porosimeter (AutoPore III, Micromeritics, USA). Before analysis samples were dried at 105 °C for 24 h on air.

XPS measurements were carried out using the ESCAProbeP (Omicron Nanotechnology) spectrometer equipped with monochromatic Al K_α X-ray source (1486.7 eV) and hemispherical electron analyzer. Sample information was determined in vacuum (10^{-10} mbar) at measuring area with diameter 1 mm from surface layer 5–10 nm. The detection limit of analyzer was 0.1 atom.%, accuracy of binding energies ±0.2 eV. For component detection the NIST X-ray Photoelectron Spectroscopy Database was used.

The field emission scanning electron microscope S-4800 Hitachi (Japan) was used for the study of the TiO_2 particle morphology and the porous network topography.

The purity (carbon content in wt.%) of powders was specified on the Vario EL III apparatus from Elementar. TiO_2 powder (approximately 5 mg) was burned in oxygen atmosphere at temperature up to 1200 °C. Gaseous products (N_2, CO_2, H_2O and SO_2) were purified, separated to individual components and analyzed on TCD detector. All analyses were triplicated. The detection limit of the apparatus was 0.1 abs.%.

XRD powder diffraction patterns were measured by the PANalytical-MPD diffractometer in the conventional focusing Bragg–Brentano geometry with variable slits. Ni-filtered characteristic CuK_α radiation produced by a laboratory X-ray tube was used and diffracted intensity was registered by the PIXcel PSD detector. The patterns were collected in the diffraction angle range $2\theta = 8°–140°$. In order to correct the measured diffraction line broadening effects for the intrinsic instrumental broadening of the diffractometer the NIST LaB_6 profile standard was measured in the same experimental setup.

2.3. XRD data evaluation procedure

XRD patterns of the synthesized powders were analyzed by the WPPM method [26]. Attention was focused on a phase composition and a size of coherently scattering domains (crystallites). In WPPM the diffraction data are simulated from a microstructure model. For simplicity, crystallites were assumed to have a spherical shape. It was furthermore assumed that crystallite-size, diameter D, is distributed according to the log-normal distribution [32], which is generally found to be a suitable distribution describing the size dispersion in nanopowders of ceramic particles [28,33–35].

The log-normal distribution has two parameters [32]: the median, M, and the 'multiplicative standard deviation', σ^*. In literature the values of the mean crystallite size are usually presented. The arithmetic mean crystallite diameter, $\langle D \rangle$, and the area weighted crystallite diameter, $\langle D \rangle_A$, can be easily calculated from M and σ^* (see Appendix A).

The WPPM can account the influence of the crystal structure defects as dislocations [25,31] or stacking faults. In [29] the dislocation density was evaluated in N-doped anatase nano-crystallites. However, such a proper modeling of effects induced by crystal defects is difficult and was not yet implemented for tetragonal structures in the fitting software used (MSTRUCT [36]). Hence a more simple phenomenological approach was adopted. The effect of the local lattice parameter variation (microstrain) connected with the crystal structure imperfection was simulated by a phenomenological pseudo-Voigt function, which was convoluted with other

Download English Version:

https://daneshyari.com/en/article/74560

Download Persian Version:

https://daneshyari.com/article/74560

Daneshyari.com