



# Thermal influence on the structure and photocatalytic activity of mesoporous titania consisting of $\text{TiO}_2(\text{B})$

Teruhisa Hongo<sup>a,\*</sup>, Atsushi Yamazaki<sup>b</sup>

<sup>a</sup> Department of Materials and Life Science, Faculty of Science and Technology, Seikei University, 3-3-1 Kichijoji-Kitamachi, Musashino, Tokyo 180-8633, Japan

<sup>b</sup> Department of Resources and Environmental Engineering, School of Creative Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo 169-8555, Japan

## ARTICLE INFO

### Article history:

Received 23 June 2010

Received in revised form 12 November 2010

Accepted 11 December 2010

Available online 17 December 2010

### Keywords:

Mesoporous titania

$\text{TiO}_2(\text{B})$

Anatase

Phase transition

Photocatalyst

## ABSTRACT

Mesoporous titania was synthesized using the evaporation-induced self-assembly method. The sample calcined at 300 °C had a wormhole-like structure with uniform mesopores consisting of  $\text{TiO}_2(\text{B})$ . The sample calcined at 350 °C consisted of a mixed phase of  $\text{TiO}_2(\text{B})$  and anatase; however, the mesoporous structure showed little change compared with that of the sample calcined at 300 °C because the phase transition from  $\text{TiO}_2(\text{B})$  to anatase has a displacive phase transition mechanism with no atomic diffusion and accompanying no crystallite growth. When calcined above 400 °C, the mesoporous structure collapsed, and aggregates of anatase nanoparticles that were highly crystalline and had high specific surface area were obtained because the mesopores at several nm intervals inhibit anatase particle growth. Samples calcined at 300, 350, 400, and 450 °C showed 1.5, 2.4, 2.5, and 1.8 times higher photocatalytic activity than commercial titania P-25 in acetic acid decomposition.

© 2010 Elsevier Inc. All rights reserved.

## 1. Introduction

A significant amount of attention has been paid to reveal the relationship between the morphology and properties of nanostructured materials [1–3]. Morphological control of materials involves a variety of aspects, including regulation of their shape, size, structure, pore size, and connectivity. Diverse morphologies such as particles, fibers, films, and porous structures result in different properties for various applications [4]. Since the discovery of ordered mesoporous silica materials (e.g., MCM-41) in the early 1990s [5,6], they have attracted considerable attention as catalysts, membranes, controlled delivery materials and adsorbents [7–9]. A wide range of mesoporous silica materials have been prepared using the structure-directing functions of electrostatic, hydrogen-bonding and van der Waals interactions. This approach has been extended to non-silica materials such as transition-metal oxides, metal phosphates and metal sulfates [10–12]. Mesoporous non-silica materials have attracted considerable attention, as they usually show remarkably higher surface areas, much more uniform and controllable pore sizes and pore morphologies compared with previous nanocrystalline materials; in many cases, they display unique electronic, magnetic and catalytic properties [13–16].

In the last few decades, oxides of transition metals have attracted the interest of many scientists because transitional metal

atoms are multi-valent, so they have some advantages over silicate materials [17]. As one of the most important transition-metal oxides, titania is a very interesting material because of its numerous applications, including chemical sensing, photocatalysis, catalyst support and energy conversion applications [18]. Titania with large surface area, high crystallinity and appropriate crystalline phase is typically employed in these applications. Many efforts had been devoted to the synthesis of titania with high performance characteristics.

Mesoporous titania was first prepared using a phosphate surfactant through a modified sol–gel process [19]. However, the products contained a large amount of phosphorous, and they underwent partial collapse of the mesostructure during template removal by calcination. Phosphorous-free mesoporous titania has been synthesized using an alkylamine template that can be removed by solvent extraction. In this case, however, the porous structure was not retained after heat treatment in dry air at 300 °C [20]. The synthesis of mesoporous titania with crystalline walls has proven difficult. The transformation from the amorphous phase to the crystalline phase by heat treatment usually induces a collapse of the mesopores because the wall is too thin to retain the three dimensional mesoporous structure during crystallization. Kondo and co-workers reported that ordered mesoporous Ta and Nb–Ta oxides were crystallized after reinforcement of the amorphous framework by silica or carbon [21–23]. A crystallized wall structure is expected to provide better thermal and mechanical stability, as well as superior electronic and optical properties. The crystallization, crystal phase and crystallinity of mesoporous

\* Corresponding author. Tel.: +81 422 37 3984; fax: +81 422 37 3871.

E-mail address: [peea.hongo@hotmail.co.jp](mailto:peea.hongo@hotmail.co.jp) (T. Hongo).

tania have therefore attracted a significant amount of attention. Mesoporous titania obtained with a block copolymer surfactant has been shown to possess uniform pores with dimensions of several nm in diameter and thick walls, with the latter providing high thermal stability and enabling amorphous to anatase crystallization of the pore wall [24,25]. To date, several types of mesoporous titania with crystalline walls have been reported. The crystalline phase is only anatase, although titania has some polymorphs such as rutile and brookite. The amorphous to anatase crystallization takes place above 350 °C, is always accompanied by high shrinkage of the mesostructure and is eventually followed by its total collapse at higher temperatures due to the extensive growth of anatase nanocrystals and phase transition to the rutile phase [26–28]. Recently, we succeeded in synthesizing mesoporous titania with uniform mesopores consisting of TiO<sub>2</sub>(B) [29], which is one of the titania polymorphs with a layered structure [30]. In this study, the thermal influence on the structure of the mesoporous titania consisting of TiO<sub>2</sub>(B) was analyzed. Moreover, the photocatalytic activity of the obtained samples following thermal treatment was investigated.

## 2. Experimental

### 2.1. Sample preparation

The surfactant used in this study was Pluronic P123, which is a triblock co-polymer, was obtained from BASF. The titanium source was titanium(IV) ethoxide, the source of acid was hydrochloric acid (HCl) and the co-solvent was 1-butanol, all of which were purchased from Aldrich. All of the chemical reagents used in the experiments were obtained from commercial sources at guaranteed grade and were used without further purification or treatment.

Samples were prepared by a procedure similar to that was reported in our literature [29]. Pluronic P123 (1.0 g) was dissolved in 11.0 ml of 1-butanol. Separately, 1.9 ml of HCl (37 wt.%) was added to 2.8 ml of titanium(IV) ethoxide (Ti(EtO)<sub>4</sub>), followed by stirring for an hour. These surfactant and titanate solutions were combined at room temperature and stirred for 3 h. The molar composition of the reactant solution was 1.0Ti(EtO)<sub>4</sub>:1.7HCl:0.013P123:8.9<sub>1</sub>-butanol. The solution was transferred into an open Petri dish to form a 1 mm thick liquid layer and then aged at 40 °C in air for 3 days to form a gel in an uncontrolled humidity and unventilated incubator (IC340S, Yamato Scientific. Co. Ltd.). During this process, the temperature was kept constant. After the gel was dried, the as-synthesized sample was calcined in air at 300, 350, 400, or 450 °C for 4 h at a heating rate of 1 °C/min using a platinum crucible.

### 2.2. Sample characterization

Thermogravimetric and differential thermal analysis (TG–DTA) measurements were performed at a heating rate of 1 °C/min in air using a Rigaku Thermo Plus 2 TG-8120 apparatus. The small-angle X-ray diffraction (SAXRD) patterns were obtained with a Rigaku RINT-TTR III diffractometer using CuK $\alpha$  radiation. The wide-angle X-ray diffraction (WAXRD) patterns were obtained with a Rigaku RINT-Ultima III diffractometer using CuK $\alpha$  radiation. The transmission electron microscope (TEM) observations were conducted with a JEM-1011 transmission electron microscope operated at 100 kV. N<sub>2</sub> adsorption/desorption isotherms were measured on a Micromeritics ASAP 2010 at 77 K. Samples were out gassed at 150 °C under vacuum for 5 h. Average pore diameters were calculated using the Barrett–Joyner–Halenda (BJH) method from the adsorption branch of the isotherm. The specific surface area was calculated from the

multi-point Brunauer–Emmett–Teller (BET) method. The UV–Vis spectra were measured on a JASCO V-550 spectrometer and used to estimate the band gaps.

### 2.3. Photocatalytic activity

The photocatalytic activity of the obtained mesoporous titania samples in the oxidative decomposition of acetic acid in aerated aqueous suspensions was examined. Prior to the photocatalytic reaction, pre-treatment was carried out to decompose some residual organic matter derived from thermal decomposition of the surfactant [31]. The sample (50 mg) was suspended in an aqueous solution (5.0 cm<sup>3</sup>) containing acetic acid (5.0 vol.%). The reaction was carried out in reaction tube (18 mm in diameter and 180 mm in length, transparent for light with a wavelength of >300 nm) under aerated conditions. The suspension was stirred (1000 rpm) at room temperature using a magnet bar and was irradiated with a 300 W xenon lamp (<700 nm). The amount of carbon dioxide (CO<sub>2</sub>) in the gas phase was measured at every 1 h by a Shimadzu GC-8A gas chromatograph equipped with WG-100 column.

## 3. Results and discussion

The obtained as-synthesized sample was a transparent yellowish material. The TG–DTA measurement of the as-synthesized sample showed a gradual weight loss from room temperature to approximately 400 °C, with an exothermic peak at 250 °C and a shoulder at 330 °C (Fig. 1). Considering the previous reports of the weight loss curve [32,33], which were similar to that in this experiment, the 12.0% mass loss below 120 °C was due to volatile species such as water, ethanol, butanol and HCl. Between 120 °C and 300 °C, a mass loss of 41.4% came from decomposition of the P123 template, which is well known in the literature [24]. Some residual organic matter, such as amorphous carbon or carboxylate species and possibly hydroxyl groups, was removed at temperatures between 300 °C and 400 °C, with a mass loss of 6.2%. Above 400 °C, the mass loss was negligible.

The calcined samples were investigated by SAXRD measurements (Fig. 2). The SAXRD patterns of the samples calcined at 300 and 350 °C showed a single broad peak corresponding to *d* values of 7.7 and 7.1 nm, respectively, which were suggestive of mesostructural order. The SAXRD pattern of the sample calcined at 400 °C showed an obvious peak shift to lower angles at a *d* value of 12.1 nm. The *d* spacing was found to be about 57% expansion

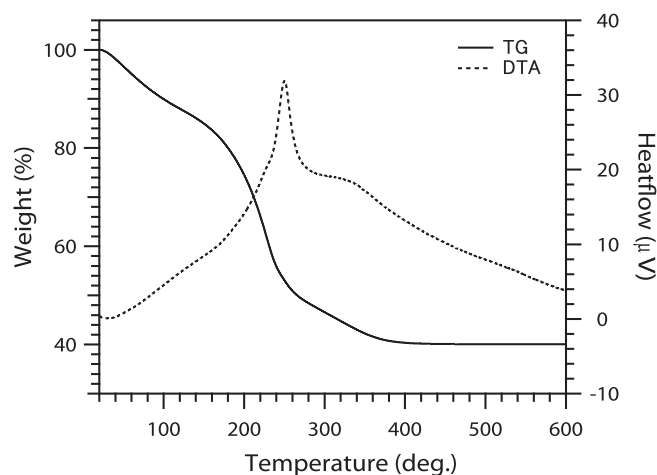


Fig. 1. TG–DTA curve of the as-synthesized sample.

Download English Version:

<https://daneshyari.com/en/article/74651>

Download Persian Version:

<https://daneshyari.com/article/74651>

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