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Comparative examination of titania nanocrystals synthesized by peroxo titanic acid approach from different precursors

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Abstract

Titanium dioxide nanocrystalline particles were synthesized by peroxo titanium acid (PTA) approach from titanium alkoxide and inorganic salt precursors, and their structural and surface properties, porosities, and photocatalytic activities were comparatively examined by XRD, TG/DTA, DRIFT, UV–vis, low temperature N_2 adsorption, and methyl orange (MO) degradation. It was found that nanoparticles with single anatase phase can be obtained from alkoxide precursor even near room temperature if synthesis conditions are appropriately controlled. PTA-derived anatase nanoparticles from titanium alkoxide precursor have smaller crystalline sizes and better porosities, and contain less amount of peroxo group and no organic impurities as compared to those from $TiCl_4$ precursor. The advantages in structural property, porosity, and surface properties (few deficiencies) lead to a much better photocatalytic activity for TiO_2 nanoparticles from titanium alkoxide precursor in comparison with those from $TiCl_4$ precursor.

Keywords: Titania; Nanocrystal; Chemical synthesis; Characterization; Photocatalytic activity

1. Introduction

Nanocrystalline titanium dioxide has received much attention for its high photocatalytic activity toward many organic pollutants in environment [1,2]. The photocatalytic activity of titania is dependent not only on its crystalline phases and sizes but also on its morphology, surface properties, porosities, and so forth [3–5]. It is well known that the metastable anatase-type TiO_2 exhibits excellent photocatalytic activity among the three polymorphs of anatase, rutile, and brookite. Pure anatase titania can be prepared by the ordinary sol–gel method [6–10] or recently by the peroxo titanic acid (PTA) approach [11–14]. The sol–gel method using alkoxide precursors is a popular and effective way to obtain anatase particles because of easy hydrolyzing properties of alkoxide. However, this method generally requires acid or base catalysts, and anatase sols thus obtained are stabilized in acid or basic solution which makes them difficult for such applications as film formation on corrosive surface. By the contrast, PTA approach gives pure anatase by oxidizing amorphous titanium oxide/hydroxide precipitates using hydrogen peroxide, followed by a hydrothermal treatment or calcination. In comparison with the sol–gel method, PTA approach is of great importance because it brings about pure anatase powder or anatase sol at a relatively low temperature and under a neutral pH condition.

In previous researches, inorganic Ti salts such as $TiCl_4$, $TiOSO_4$, etc. are usually applied as precursors in the PTA approach [11–26]. However, anatase products obtained from these precursors easily contain impurities such as NH_4^+ (from the neutralization agents, NH_4OH) or the peroxo group

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–O–O– [11]. Some previous researches have tried to use titanium alkoxide as a precursor in PTA approach, but titania products from these methods tend to be of rutile phase or the mixed phase of anatase and rutile [27,28]. It was reported that additional organic species such as alcohol are necessary to obtain pure phase anatase particles by using alkoxide as a precursor in PTA approach [29–31]. In a previous letter, we have reported that, by a simple procedure appropriately controlling the synthesis condition, nanoparticles with single anatase phase can be obtained from alkoxide precursor even near room temperature and without using any extra organic species [32]. In this paper, we synthesized PTA-derived titania nanocrystals at various conditions using alkoxide as a precursor and extensively examined their structural and surface properties, porosity, and photocatalytic activity. These properties were compared with those from typical inorganic salt precursor and those using alkoxide precursor but the ordinary procedures.

2. Experimental

2.1. Preparation of samples

Ichinose's method [11] was applied to the sample preparation except some modification when using titanium tetraisopropoxide ($Ti(i\text{-}OC_3H_7)_4$) precursor. $TiO(OH)_2$ precipitates were first obtained by dripping 2.84 g $Ti(i\text{-}OC_3H_7)_4$ into 100 ml de-ionized water (d.w.) without adding any solvent or acid/base catalysts. The precipitates were washed several times with d.w. and then filtered to remove organic byproducts and d.w. Next, PTA solution was obtained by adding 30% H_2O_2 solution into the wet $TiO(OH)_2$ precipitates powders at a molar ratio of H_2O_2/titanium = 10 under vigorous agitation. A clear solution with a deep orange color was formed immediately after H_2O_2 addition and the exothermic reaction leads to radical bubbling. Once bubbling occurs, the solution was soon moved into an ice bath so as to make the solution cooling down to room temperature (RT). Then the ice bath was moved out again, allowing reaction continuing at RT. This cooling process was repeated until no bubbles released from the solution at RT. Titania nanoparticles (PTA-A-T where T denotes the calcination temperature) were obtained by evaporating water from the PTA solution at 333 K and by further calcination at different temperatures in air for 2 h. For examination of the effect due to the cooling process, samples (PTA-A-T-nc) using the above procedure, however, without the cooling process were also prepared.

For comparison, samples using $TiCl_4$ precursor were also prepared following the Ichinose's method [11]. Briefly, $TiO(OH)_2$ precipitates were first obtained by adding ammonia solution (10%) into $TiCl_4$ aqueous solution (0.1 mol/L). The final pH of the solution after precipitation was adjusted to be 7. The precipitates were washed several times with d.w. until chlorine ions were not detected by $AgNO_3$ solution. Subsequently, H_2O_2 solution was added into the wet $TiO(OH)_2$ precipitates, allowing the gas-releasing reaction to proceed. This process was maintained around RT using the same cooling procedure as that for preparation of PTA-A-T. After complete release of bubbles, the PTA solution with a bright yellow color was obtained. The finial titania particles (PTA-B-T) were obtained by evaporating water from the PTA solution and further calcination in air at temperature T for 2 h.

2.2. Characterization

X-ray diffraction patterns (XRD) of samples were measured by a Rigaku Co.-made RU-300 system using CuK_α radiation ($\lambda = 0.15406$ nm) in the 2θ range of 10°–80°. The operating tube voltage and current were 40 kV and 80 mA, respectively. Data were collected at a scanning speed of 2°/min and a sampling angle interval of 0.02°. The thermal gravimetry (TG) and differential thermal analysis (DTA) measurements were carried out by a Rigaku Co.-made Thermo 2000 TG/DTA system under curtain gas of air with a constant flow rate of 100 ml/min. Temperature was raised from room temperature to 1073 K at a ramp rate of 10 K/min. The diffuse reflectance infrared Fourier transform (DRIFT) spectra of samples were measured by a Nicolet NEXUS 470-type FT-IR spectrometer with a MCT detector. Each spectrum was recorded from 256 scans at a resolution of 2 cm^{-1} after CO_2 impurities completely disappear from the spectra through continuous purge of nitrogen gas of 99.99% purity. The diffuse reflectance UV–vis spectra (DRS) of samples were measured by a JASCO Co.-made V-650 type UV–vis spectrometer equipped with an integration ball and by using $BaSO_4$ as the reference. The nitrogen adsorption isotherms were measured at 77 K by a Belsorp Co.-made Belsorp 18A-type volumetric apparatus. Samples were degassed under vacuum at 393 K for 2 h before adsorption.

2.3. Photocatalytic reaction

Methyl orange (MO) was used as a model organic material to examine photocatalytic activities of samples. 10 mg sample was placed into an Erlenmeyer tube containing 20 ml MO solution with an initial concentration (C_0) of 50 mg/L. The tubes were then hermetically sealed with a quartz cover for penetration of UV light and immersed in a water bath having a constant temperature of 303 K. After continuous vibration under dark condition for 24 h to allow adsorption equilibrium, photocatalytic reaction start on by switching on black lights (6 × 15 W) situated on the top of the water bath. After reaction for a certain time interval, the corresponding tube was taken out and the solution was separated by centrifugation. The MO concentration (C) in the collected solution was measured by a JASCO Co.-made V-650 type UV–vis spectrometer using absorbance at 450 nm.

3. Results and discussion

3.1. XRD patterns

Fig. 1 compares the XRD patterns of PTA-A-T, PTA-A-T-nc, and PTA-B-T with different T. In contrast to in the XRD patterns of PTA-B-333 and PTA-A-333-nc where no peak or ambiguous peak can be observed, that of PTA-A-333 shows an evident peak at $2\theta = 25.34°$ due to diffraction of the (101) plane