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Effects of reaction medium and crystallite size on Ti^{3+} surface defects in titanium dioxide nanoparticles prepared by solvothermal method

Akawat Sirisuk, Ekkachai Klansorn, Piyasan Praserthdam *

Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering,
Faculty of Engineering, Chulalongkorn University, Phayathai Road, Patumwan, Bangkok 10330, Thailand

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Abstract

Titanium dioxide nanoparticles were prepared using solvothermal methods in 1,4-butanediol and toluene. Three different crystallite sizes (10 nm, 13 nm, and 17 nm) of titania as anatase crystals were produced and were then employed as catalysts in photocatalytic oxidation of ethylene in gas phase. As the crystallite size of titania increased, more Ti^{3+} surface defects were observed. The amounts of surface defects on titania were determined by temperature-programmed desorption using carbon dioxide as a probe molecule. Despite the smaller specific surface area, titania with larger crystallite size exhibited higher photocatalytic activity, which was attributed to more surface defects in the catalyst.

Keywords: Titanium dioxide; Solvothermal method; Surface defects; Photocatalysis; Ethylene oxidation

1. Introduction

Titanium dioxide or titania has been a subject of extensive study as a photocatalyst. Titania has several advantages when employed as a photocatalyst. Titania displays high photocatalytic activity for a variety of reactions and exhibits chemical stability and resistant to photocorrosion when in contact with various solvents [1]. Application of titania in photocatalytic reactions includes splitting of water [2,3], mineralization of organic compounds in water [4,5], synthesis of organic chemicals [6], removal of environmental pollutants from atmosphere [1,5], and treatment of indoor air [7].

Several factors can influence photocatalytic activity of titania. These factors include particle size, specific surface area, and crystal structure [1,8–11]. As catalyst particles become smaller, specific surface area of a catalyst increases and hence a greater number of active surface sites and higher transfer rate of surface charge carrier. However, in the case of nanocrystalline titania photocatalyst, the photocatalytic activity does not increase monotonically with decreasing particle size because the benefits from high surface area are offset by the increased recombination rate of electron–hole pairs at the surface of the nanoparticles [10].

Titanium dioxide crystal always contains structural defects both on the surface and inside the bulk of the particles [12]. These defects are involved in trapping of photogenerated electrons in titania particles when being exposed to irradiation with appropriate wavelengths [13,14]. Bulk defects act as recombination centers for electron–hole pairs, thereby decreasing photocatalytic activity of titania [15,16]. Heat treatment at high temperature can be applied to the photocatalyst in order to reduce the amount of bulk defects in the crystal and bring about higher photocatalytic activity of the catalyst [16]. Surface defects in titania crystals are a result of surface oxygen vacancies, which leave Ti^{3+} sites exposed [17,18]. Ti^{3+} sites play an essential role in photocatalytic process over titania photocatalyst. Temperature-programmed desorption (TPD) using carbon dioxide as a probe can be employed to monitor surface defects on titania [19,20]. Surface oxygen vacancies (Ti^{3+}

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* Corresponding author. Tel.: +66 2218 6766; fax: +66 2218 6877.
E-mail address: piyasan.p@chula.ac.th (P. Praserthdam).

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sites) bind carbon dioxide slightly more strongly (TPD peak at 166 K) than do the five-fold coordinated Ti^{4+} sites (TPD peak at 137 K).

In this paper, titania nanoparticles were synthesized using solvothermal methods in organic solvents. The two solvents employed (i.e., 1,4-butanediol and toluene) were shown to bring about different routes in formation of titania nanocrystals [21]. An attempt was made to relate the photocatalytic activities of the catalysts in photocatalytic oxidation of ethylene in gas phase to the amounts of surface defects in the TiO_2 particles that had various crystallite sizes or were prepared in different reaction media. The amounts of surface defects in titania nanoparticles were quantified by temperature-programmed desorption using carbon dioxide as a probe molecule.

2. Experimental

2.1. Preparation of titanium dioxide nanoparticles

Solvothermal synthesis of titania nanoparticles was based on the procedure described by Kominami and coworkers [22]. Titanium(IV) *n*-butoxide (TNB) was employed as a precursor for titania. A certain amount of TNB, ranging from 7.5 g to 25 g, was added to 100 ml of organic solvent in a test tube. Two different organic solvents, namely, 1,4-butanediol and toluene, were used in the synthesis. The test tube was then placed in an autoclave reactor with a volume of 300 ml. The gap between the test tube and the wall of the autoclave reactor was filled with 30 ml of an organic solvent of the same type. The autoclave reactor was sealed and purged completely with nitrogen. The temperature of the reactor was then raised to a desired level, ranging from 300 °C to 320 °C, at a rate of 2.5 °C/min and was held constant for the duration of time, ranging from 30 min to 6 h. Autogeneous pressure was generated during the increase of the temperature of the reactor. After the autoclave reactor was cooled to a room temperature, the resulting titania particles were washed repeatedly with methanol and were dried in ambient air.

2.2. Characterization of titanium dioxide nanoparticles

Powder X-ray diffraction (XRD) analysis was performed using a Siemens D5000 X-ray diffractometer that employs Cu Kα radiation ($\lambda = 1.54439$ Å). The scan rate was 0.04°/min in the 2θ range between 20° and 80°. The crystallite size of titania was estimated from the line-broadening of its main anatase (1 0 1) peak according to the Scherrer equation. Specific surface area of the samples was determined from nitrogen adsorption using the BET single-point method.

Temperature-programmed desorption (TPD) was carried out using carbon dioxide as a probe molecule. Cryogenic temperature in the range between −150 °C and 0 °C was achieved using liquid nitrogen and was controlled manually. The signal of carbon dioxide released during desorption was detected using a Gow Mac (series 150) gas chromatograph that was equipped with a thermal conductivity detector.

2.3. Photocatalytic oxidation of ethylene

Photocatalytic oxidation of 0.1% (*v*/*v*) ethylene in balance air was carried out in a horizontal quartz tube with an inner diameter of 1 cm. First, 0.4 g of titania nanoparticles was spread along the inner surface of the tube. The length of the spread of the catalyst is approximately 9 cm. Quartz glass wool was inserted at both ends of the tube in order to seal the reactor. A 500 W high-pressure mercury lamp was employed as an irradiation source and was located directly above the tube. The distance between the lamp and the reactor was 20 cm. The light irradiance at the surface of the reactor was approximately 0.65 mW/cm^2.

At the beginning of each experiment the reactor was supplied with air at a flow rate of *ca.* 60 ml/min and was exposed to ultraviolet irradiation for 1 h. The purpose of this step is to remove any compounds that might remain from previous experiments from the surface of the catalyst. After 1 h, a gas stream containing 0.1% (*v*/*v*) ethylene in balance air was fed to the reactor at a flow rate equal to *ca.* 10 ml/min. Samples of effluent gas were taken at every 30 min interval until the duration of the experiment reached 4 h. The concentrations of ethylene in the feed and effluent streams were determined using a Shimadzu GC14B gas chromatograph that was equipped with a flame ionization detector. The column used was a Shimadzu VZ-10 column.

3. Results and discussion

3.1. Synthesis and physical characterization of titanium dioxide nanoparticles

To obtain titania nanoparticles of desired crystallite size, three variables in solvothermal synthesis, namely, concentration of precursor (i.e., TNB), temperature of reaction, and holding time for reaction, were adjusted. Table 1 shows the conditions under which titania nanoparticles were prepared in each of the two different solvents (i.e., 1,4-butanediol and toluene). The resulting particles were titania nanoparticles with crystallite sizes of 10 nm, 13 nm, and 17 nm, respectively. The XRD patterns, as shown in Fig. 1A and B, suggest that the titania nanoparticles obtained are anatase phase without contamination of other phases such as rutile or brookite. Average crystallite sizes of the nanoparticles were calculated from the broadening of the (1 0 1) peak of the anatase phase. Our previous study [21] confirmed that the crystallite sizes determined from the XRD patterns were in good agreement with inspections of images obtained from transmission electron microscope and the size distribution was narrow.