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A novel adsorbent photocatalyst consisting of titania and mesoporous silica nanoparticles

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Abstract

The nanoscale combination of crystalline titania and mesoporous silica particles was successfully applied as a photocatalytic adsorbent for the rapid removal from air and complete decomposition of organic molecules. The composites consisted of anatase particles ca. 7 nm in diameter and mesoporous silica particles 10–100 nm in diameter, which provided a specific surface area of more than 1000 m^2/g. The composites were prepared through the assembly of surfactant micelles and siliceous species in the presence of the titania nanoparticles. Acetaldehyde was quickly removed from air due to the large surface area of the mesoporous silica and then was gradually decomposed into carbon dioxide under UV illumination with mass transfer between the adsorbent and the titania photocatalyst.

Keywords: Titania; Mesoporous silica; Composite; Adsorbent; Photocatalyst

1. Introduction

Titania photocatalysts have received much attention in regard to their application to environmental purification because the photocatalytic reaction can decompose many kinds of organic contaminants in air and water [1]. Many studies have addressed the preparation of titania with a high specific surface area to improve catalytic activity [2–5]. The synthesis of titania particles with a specific surface area of more than 300 m^2/g has been successfully performed [5]. However, high performance is not always obtained with a high specific surface area because a decrease in the grain size is generally accompanied by a degradation of the crystallinity and an increase in the number of defect sites. Recently, titania was mixed with porous materials as an adsorbent to improve total purification because contaminants were temporarily reserved on the adsorbent [6–15]. In this system, rapid adsorption covered the low reaction rate of photocatalysis. Zeolite [6] and hydroxyapatite [7,8] have been applied as adsorbents for the composite photocatalysts. However, the specific surface area is insufficient for the adsorption of a large number of organic molecules. Moreover, the mass transfer from adsorbents to titania is another problem for mixture-type photocatalytic adsorbents. Thus, a nanoscale combination of titania and mesoporous silica is required for smooth mass transfer. Mesoporous silica prepared using surfactants as templating agents is a suitable candidate for a porous substrate because of the high specific surface area and high transparency in the UV region [16]. Previously, the framework of mesoporous silica modified with titanium ions has been reported [9–11]. However, high photocatalytic activity was not obtained with modified mesoporous silica because of the coarse crystal structure of titania in the silica framework. Therefore, the co-existence of titania with high crystallinity and mesoporous silica with smooth mass transfer would be suitable as an adsorbent photocatalyst. Although coating of titania on the surface of the pores of mesoporous silica was achieved [12–14], the surface area of the composites decreased because the titania filled the mesopores. A nanocomposite of titania particles and mesoporous silica has been reported by Inumaru et al. [15]. In their work, titania nanoparticles 20–30 nm in diameter were incorporated into large particles of mesoporous silica. The composites were produced as a molecular selective photocatalyst and showed selective decomposition of 4-nonylphenol. In this case, the mesoporous silica which provides the molecular selectivity was not utilized as an adsorbent of the reactants.

Here, we propose a new type of adsorbent photocatalysis using nanoscale composites consisting of small particles of titania ca. 7 nm in diameter and mesoporous silica 10–100 nm in

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diameter. Nanoscale composites consisting of titania and mesoporous silica nanoparticles had a sufficient activity as a photocatalyst and a large surface area as a adsorbent with a smooth mass transfer from silica to titania. Therefore, the nanocomposites were found to be functioned reliably for environmental purification.

2. Experimental

The preparation method was based on the technique for the grain-size control of mesoporous silica with the variation of the surfactant concentration reported by Ikari et al. [17]. In this method, the particle size varied from 10 to 100 nm because of the suppression effect of the excess surfactant. Although the experimental process was similar to that of the method used by Inumaru et al. [15], the particle size of our products was much smaller than that of the previous work. On the other hand, the ordered arrangement was deformed as the particle size decreased. Here, the smaller size of mesoporous silica was emphasized rather than the ordered arrangement of the mesopores as an adsorbent for the nanocomposite. Therefore, we adopted the experimental condition for the preparation of mesoporous silica nanoparticles with a diameter below 100 nm. Commercially available anatase nanoparticles with a diameter of ca. 7 nm (Ishihara ST-01) were initially added to the precursor solution. In a typical synthesis procedure, 2.6 g cetyltrimetylammonium chloride (CTAC, Kanto Chemical), 0.067–0.67 g (molar ratio Ti/Si = 0.05–0.50) titania nanoparticles, and 3.5 g tetraethoxysilane (TEOS, Kanto Chemical) were added to 30 g of water with stirring for 1 h at room temperature, and then 3.0 g ammonia water (NH_4OH, 28 wt%, Junsei Chemical) was mixed in to promote gelation. Pure mesoporous silica was also prepared using the typical procedure in the absence of titania. The resultant gel was aged at room temperature for 24 h, dried at 333 K in air for 24 h, and finally calcined in air at 873 K for 3 h to remove the organic compounds.

X-ray diffraction (XRD) patterns were measured with a Rigaku RAD-C system with Cu Kα radiation. Transmission electron micrographs (TEM) were obtained using a FEI TECNAI F20. Nitrogen adsorption and desorption isotherms were recorded at 77 K with Micromeritics TriStar3000 using samples pretreated over 2 h at 433 K. The pore size distribution and the specific surface area were calculated by the BJH and BET methods, respectively. Diffuse reflection spectra (DRS) of powdery sample were measured in the range of 200–600 nm with a JASCO UV–vis spectrophotometer V-560 with MgO as a reference sample.

The performance of adsorption and photocatalysis of the nanocomposite materials was evaluated according to the adsorption and decomposition of acetaldehyde in air with 5.0 g samples placed in a closed vessel 6 dm^3 in volume. Pure anatase (ST-01) and a mechanical mixture prepared with ST-01 and pure mesoporous silica in a mortar (Ti/Si = 0.05) were used as a reference sample. The concentrations of acetaldehyde and carbon dioxide were monitored with a Shimadzu GC-8A gas chromatograph. The initial concentration of acetaldehyde was fixed at 1500 ppm. Initially, the adsorption was measured in the dark for 3 h after the addition of acetaldehyde into the vessel, and then decomposition under illumination with a conventional black light was performed ($6\,W \times 2$, $0.1\,mW/cm^2$).

3. Results and discussion

Fig. 1 shows typical TEM images of a prepared nanocomposite (Ti/Si = 0.5). Fine particles less than 10 nm in diameter were observed in an aggregation of mesoporous silica particles 20–100 nm in diameter. The lattice fringes of the fine particles corresponding to (1 1 2) planes of anatase indicate that crystalline titania and mesoporous silica were homogeneously compounded at the nanometer level. The XRD patterns in a high-angle region also indicate that the crystal structure and crystallinity of titania nanoparticles did not change after calcination at 873 K. Fig. 2 shows bimodal pore size distributions of pure mesoporous silica and a composite (Ti/Si = 0.5). A sharp distribution around 3 nm is ascribed to a structural mesopore produced by the templating of the surfactant micelle. Relatively large mesopores ranging from 20 to 100 nm were attributed to the interparticle spaces among the mesoporous silica nanoparticles. In the case of the composites containing titania particles, the structural mesopores were maintained without deformation. On the other hand, the interparticle spaces decreased because the titania nanoparticles filled the space. Table 1 shows the specific surface area of mesoporous silica, titania, and silica–titania composites. The pure mesoporous silica had the highest surface

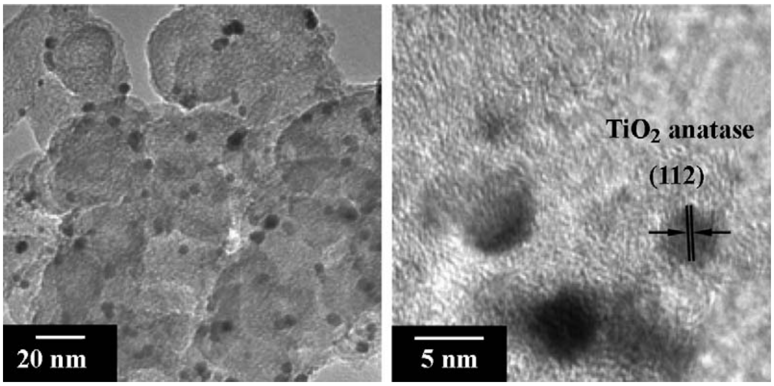

Fig. 1. TEM images of a typical composite photocatalyst (Ti/Si = 0.50).