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Development of surface coating technology of TiO_2 powder and improvement of photocatalytic activity by surface modification

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Abstract

We have synthesized the titanium dioxide (TiO_2) powders with the similar structure as a commercially available Degussa P-25 TiO_2 powder for TiO_2-based photocatalysts. To improve the photocatalytic activity, electronic modification on the TiO_2-based photocatalysts by chemical solution deposition (CSD) coating was also carried out with metal oxides such as Fe_2O_3 and Al_2O_3. The structural and compositional changes as well as optical characteristics are mainly investigated by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), UV-visible spectroscopy, and ellipsometry measurements. In addition, electron spin resonance (ESR) studies have also been carried out to verify the existence of paramagnetic species such as OH and H_2O radicals on UV-irradiated TiO_2-based photocatalysts. ESR data showed that the hydroxy radicals could decompose organic pollutants into harmless products because they have high oxidizing power. From the reduction test of nitrobenzene, it is found that the photocatalytic effect of TiO_2-based photocatalysts coated with Fe_2O_3 is twice better than that of commercially available noncoated TiO_2 photocatalysts. In the case of photocatalytic oxidation reaction of phenol under UV irradiation, moreover, the experimental results showed a consistency with ESR data indicating that TiO_2 coated with metal oxides would be one of the most effective photocatalysts.

Keywords: TiO_2-based photocatalysts; Surface modification; Chemical solution deposition; Photocatalytic reduction–oxidation reaction; Electron spin resonance analysis

1. Introduction

Titanium dioxide (TiO_2) has been known as a useful photocatalytic material because it is photosensitive, stable, and inexpensive [1–5]. There is a growing interest in recent years to find new, efficient, and economic methods to clean up the environment of pollution materials. This is inspired by the potential application of TiO_2-based photocatalysts for the total destruction of organic compounds in polluted air and wastewater.

The bulk material of TiO_2 is well known to have three main phases namely rutile, anatase, and brookite [6]. Among them, the TiO_2 exists mostly as rutile and anatase phases and both phases have tetragonal structures. Rutile is a high-temperature stable phase and has an optical energy band gap of 3.0 eV (415 nm), while anatase is formed at a lower temperature with an optical energy band gap of 3.2 eV (380 nm) as well as refractive index of 2.3 [7]. It is well known that generally, the TiO_2-based photocatalyst with anatase phase shows more excellent photocatalytic effect than that with rutile phase, and the anatase phase can be transformed into the rutile phase at above 800 °C [8,9]. The role of the holes and electrons at the surface of TiO_2 in heterogeneous photocatalysis has been investigated in aqueous suspension for the reduction–oxidation (redox) reaction of several organic compounds [10–14]. Electron spin resonance (ESR) studies have been carried out to verify the existence of paramagnetic species such as $\cdot OH$ and $HO_2\cdot$ on UV-irradiation of TiO_2 [5,14–19]. However, the photophysical mechanism of surface-modified TiO_2 pow-

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ders by metal oxides is not well understood yet. Electronic modification of the photocatalyst by coating of metal oxides such as Fe_2O_3, Al_2O_3, MoO_2, and MoO_3 has a strong effect on the photoreactivity of the system. The efficiency of electron-hole separation and the dynamics of interfacial electron transfer can be dramatically influenced. Various synthetic methods and coating techniques have been developed for development and modification of the TiO_2-based photocatalysts including chemical vapor deposition (CVD), metal–organic chemical vapor deposition (MOCVD), and sol–gel methods [20,21].

In this study, therefore, we have synthesized the TiO_2 powders with the similar structure as a commercially available Degussa P-25 TiO_2-based photocatalysts using both slurry of metatitanic acid and sol–gel method. We have also developed a surface modification technology of TiO_2-based photocatalysts by chemical solution deposition (CSD) for improving their photocatalytic activity. To investigate the effects of surface modification by CSD and annealing, moreover, we mainly studied the structural and compositional changes of the TiO_2 powders as well as optical characteristics with X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), ESR, UV-visible spectroscopy (UV-Vis), and ellipsometry measurements because the electronic modification of the photocatalysts by CSD has a strong effect on the photoreactivity of the TiO_2-based photocatalysts.

2. Experimental

TiO_2 powders were synthesized by a slurry reaction of metatitanic acid [$TiO(OH)_2$] and ethyl alcohol. After ball milling of them for 24 h, the slurry was kept at the temperature of 110 °C for further 24 h in the oven for evaporation of the alcohol, and then annealed at 600 °C for 2 h, resulting in a TiO_2 powder formation with 58 m^2/g of BET surface area and 87 nm of average particle size, respectively. The synthesized TiO_2 powders have the similar structure and surface area as the commercially available Degussa P-25 TiO_2 powders (rutile/anatase=3:7; surface area=55 m^2/g) [20]. Moreover, a coating sol for TiO_2-based photocatalysts was also prepared by the sol–gel method, using titanium tetraisopropoxide, acid (HCl, HNO_3, HF, etc.), and water. Titanium tetraisopropoxide was slowly dropped into the 0.4% nitric acid solution after stirring it vigorously for 2 h at room temperature, and then heated at 80 °C for 24 h. During the reaction, isopropanol was removed by distillation and then the milky–bulk reaction solution was gradually changed to blue fine–milky solution. TiO_2 coating sol was cooled at room temperature, then colloidal SiO_2 and tetraethoxyorthosilicate (TEOS) were added to this solution, stirring for 5 h. To improve their photocatalytic activities, electronic modification on the TiO_2-based photocatalysts by CSD was also carried out with metal oxides such as Fe_2O_3 and Al_2O_3. In addition, in order to understand the detailed mechanism of photocatalytic reduction–oxidation reactions, electron spin resonance (ESR) studies have also been carried out.

3. Results and discussion

Fig. 1(a) shows the X-ray diffraction pattern of TiO_2 powders synthesized by a reaction of titanium tetraisopropoxide, acid (HCl, HNO_3, HF, etc.), and water and then annealed at different temperatures in air. In the sample annealed at 300 °C, the powder has in part a nature of anatase crystal structure. With increasing annealing temperature to 600 °C, the crystallinity of the TiO_2 powder was increased because the characteristic TiO_2(101) diffraction peak with anatase structure becomes stronger than that of 300 °C. However, a new diffraction peaks due to a phase transition from anatase phase to rutile phase also appeared in the TiO_2 powder after it was annealed at 1000 °C. By measuring the relative peak intensity of their main diffraction peaks of (b) and (c), the abundance ratio of rutile and anatase phases that were confirmed by XPS (not shown here) can be deducted to be rutile/anatase=5:5. Comparing Fig. 1(a) with Fig. 1(d), that is, XRD pattern of commercially available Degussa P-25 TiO_2 powder, one can identify the difference of the abundance ratio with annealing temperature. It is well known that the abundance ratio of Degussa P-25 TiO_2 powder, which is now the most excellent photocatalyst in the world, has a rutile to anatase ratio of 3:7. Thus, it is highly desirable for us to make the TiO_2 powder with the same abundance ratio as Degussa P-25 TiO_2 powder as well as similar crystallinity by controlling the annealing temperature, reactive gas, and surface area with near by the same particle size.

To make the best photocatalysts, we also did surface modification of the synthesized TiO_2 powders by CSD coating with metal oxides such as $Fe_2O_3(Fe^{3+})$ and $Al_2O_3(Al^{3+})$ for improving their photocatalytic activity for total destruction of organic compounds in waste solvents. Fig. 1(b) and (c) shows the XRD patterns of TiO_2 powders obtained after 0.1% Fe_2O_3 (b) and 0.1% Al_2O_3(c) coatings annealed at different temperatures. Below 600 °C annealing temperature, highly oriented TiO_2 powders with pure anatase structure could be observed from both Fig. 1(b) and (c). The abundance ratio obtained from the samples was about rutile/anatase=3:7. At 1000 °C annealing temperature, however, we can see distinct difference of the abundance ratio of rutile to anatase phases after judging the relative main diffraction peaks. Although we obtained the same rutile to anatase ratio as Degussa P-25 TiO_2 powder in the case of a TiO_2 sample annealed at 600 °C, we cannot directly compare the photocatalytic activity between our synthesized TiO_2 powders and commercially available Degussa P-25 TiO_2 powder with rutile to anatase ratio only. Therefore, we measured the ESR spectra and tried surface modification of our synthesized TiO_2 powders using annealing or chemical solution deposi-