Degradation of organic compounds on TiO₂ photocatalysts prepared by a hydrothermal method in the presence of NH₄F

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Abstract TiO₂ photocatalysts were synthesized by a hydrothermal method from tetraisopropyl orthotitanate (TPOT) in the presence of NH₄F with different NH₄F/Ti molar ratios (0, 0.25, and 1). The formation of a well-crystallized anatase phase of TiO₂ and the suppression of phase transition to rutile were observed, even at high calcination temperature, owing to the effects of NH₄F. The TiO₂ synthesized hydrothermally with NH₄F exhibited absorption with a shift to the longer wavelengths of the visible-light region. The hydrothermally synthesized TiO₂ with a moderate amount of NH₄F exhibited high photocatalytic activity for the degradation of alcohol diluted in water under both UV-light and visible-light irradiations.

Keywords TiO₂ · Photocatalyst · Degradation · Hydrothermal method · NH₄F

Introduction

The photocatalytic degradation of organic pollutants diluted in water using TiO₂ is of vital interest. TiO₂ is a promising photocatalyst because of its low cost and nontoxicity, as well as strong oxidation ability under UV-light irradiation [1]. To realize the practical application of a TiO₂ photocatalytic system, various modifications of TiO₂ have been investigated to increase the photocatalytic activity under

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not only UV-light but also visible-light irradiation [2]. Because the highly crystallized TiO_2 without the defect sites were found to be effective photocatalysts, the hydrothermal synthesis of TiO_2 has been applied using organic solvents [3]. The implantation of metal cations, such as Fe, Cr, and V, has been found to be effective at modifying TiO_2 into a visible-light-sensitive photocatalyst [4]. Recently, as a cheap method, Asahi et al. also demonstrated that the doping of nitrogen into TiO_2 provided the visible-light responsibility [5]. On the other hand, the doping of F^- ions within the TiO_2 lattice using NaF as a fluorine source showed enhancement in the photocatalytic activity [6–8]. The introduction of F^- ions is also showing promise to reduce the hydrophilic nature of the TiO_2 particle surface, which could enhance the affinity of the TiO_2 surface toward organic compounds by the replacement of surface $-\text{OH}$ group by F^- . The modification of the hydrophilic TiO_2 surface could also be achieved by HF or F_2 treatment.

In the present study, TiO_2 fine powder was synthesized by hydrothermal conditions in the presence of NH_4F (HT- TiO_2). The effects of NH_4F on the photocatalysis of HT- TiO_2 have been investigated for the photocatalytic degradation of alcohols (*i*-BuOH, 2-PrOH) diluted in water under UV-light and visible-light irradiations.

Experimental

TiO_2 fine powder was synthesized by the hydrothermal method using tetraisopropyl orthotitanate (TPOT: $\text{Ti}(\text{OC}_3\text{H}_7)_4$) as the starting material in the mixed NH_4F - H_2O -ethanol solution with molar ratios of $\text{Ti}:\text{H}_2\text{O}:\text{EtOH} = 1:5:5$. $\text{NH}_4\text{F}/\text{Ti}$ molar ratios were 0, 0.25, and 1. The above mixture was transferred into an autoclave and kept at 433 K for 48 h. After centrifugation, washing, drying, and calcination at 823 K for 5 h, TiO_2 powder was obtained. The products were denoted as HT- $\text{TiO}_2(0)$, HT- $\text{TiO}_2(0.25)$, and HT- $\text{TiO}_2(1)$, respectively. TiO_2 was also prepared by the conventional sol-gel method with a mixture of TPOT, H_2O , and EtOH (1:5:5) after stirring at room temperature for 24 h and then heating at 358 K for 24 h. After centrifugation, drying, and calcination at 823 K for 5 h, the sol-gel- TiO_2 was obtained.

X-ray diffraction (XRD) patterns of all samples were measured using Rigaku RINT2500 diffractometer with Cu $K\alpha$ radiation. By using an ASAP 2000 system (Shimadzu), the Brunauer, Emmett, Teller (BET) method was applied for the determination of the specific surface area. The diffuse reflectance absorption spectra were recorded with a Shimadzu UV-2200A photospectrometer. X-ray photoelectron spectroscopy (XPS) was recorded with a JEOL microprobe system using the Mg $K\alpha$ line.

The photocatalytic activity of TiO_2 was evaluated by the photodegradation of alcohol (*i*-BuOH, 2-propanol) diluted in water. 0.05 g of catalyst was placed in a quartz cell with 25 ml of aqueous alcohol solution (2.61 mmol l^{-1}). After stirring under dark conditions for 30 min, the solution was bubbled by oxygen for another 30 min. Then, the solution was irradiated under UV-light ($\lambda > 280 \text{ nm}$) or visible-light from a 100-W high-pressure Hg lamp. The reactions were monitored by gas

chromatography analysis (GC-14B, Shimadzu). Water adsorption isotherms of the catalysts were measured at 293 K using a conventional vacuum system.

Results and discussion

Figure 1 shows the XRD patterns of the hydrothermally synthesized TiO₂ (HT-TiO₂) and the sol-gel synthesized TiO₂ (sol-gel TiO₂) calcined at 823 and 923 K. The HT-TiO₂ catalysts calcined at 823 K show sharp peaks corresponding to only the anatase phase of TiO₂, but no other phases such as rutile and brookite can be detected. On the contrary, additional peaks corresponding to the rutile phase at 27.5° and 36.0° were observed in the sol-gel TiO₂. The HT-TiO₂ catalysts exhibit higher peak top intensities of the (101) peak due to the anatase phase compared to that of the sol-gel TiO₂, indicating that the TiO₂ with high crystallinity can be synthesized using hydrothermal synthesis. Among the catalysts, HT-TiO₂(0.25) exhibits the highest intensity of the (101) peak due to the anatase phase in both cases of calcinations at 823 and 923 K. The BET surface area and crystal size of these catalysts were measured as 55 m² g⁻¹ and 19.6 nm (HT-TiO₂(0)), 33 m² g⁻¹ and 23.7 nm (HT-TiO₂(0.25)), and 47 m² g⁻¹ and 21.0 nm (HT-TiO₂(1)), respectively. The results of the BET surface area and crystal size reflected the crystallinity estimated from XRD measurement. The surface area decreased with increasing crystallinity.

The XRD patterns of HT-TiO₂ and sol-gel TiO₂ calcined at 923 K are also shown in Fig. 1. The rutile phase was dominant in the sol-gel TiO₂. HT-TiO₂(0) showed the formation of the mixture of anatase and rutile phases. But with HT-TiO₂(0.25), and HT-TiO₂(1), the phase transfer to rutile was completely suppressed and all peaks could be assigned as the anatase phase of TiO₂ crystalline. It should be noted that the hydrothermal synthesis of TiO₂ from TPOT in the presence of NH₄F inhibit the phase transformation from anatase to rutile with increasing calcination temperature. F⁻ ion doping should enhance the crystallization of the anatase phase and suppress the crystallization into the rutile phase.

The F_{1s} XPS spectra of the present catalysts were measured. It was found that the F_{1s} band with binding energy at around 688 eV corresponding to the F⁻ ions in the TiO₂ lattice can be observed with HT-TiO₂(F1), while that at 684 eV is ascribed to the adsorbed F⁻ ions on the TiO₂ surface. Although the intensity of the F_{1s} was low in HT-TiO₂(F1), one major peak due to the F⁻ ions in the TiO₂ lattice was observed. On the other hand, no noticeable signals assignable to N_{1s} binding energy could be observed in HT-TiO₂(F1), suggesting that N atoms originating from the NH₄F were scarcely present.

The water adsorption isotherms of HT-TiO₂ catalysts are shown in Fig. 2. The amount of adsorbed H₂O molecules decreased on HT-TiO₂(0.25) compared to HT-TiO₂(0), which may indicate that the hydrophobic properties were generated by the replacement of the -OH group by F⁻. This result indicates that the TiO₂ synthesized in the presence of NH₄F demonstrated higher hydrophobic properties than pure TiO₂.

Fig. 1 X-ray diffraction (XRD) patterns of TiO_2 prepared by the sol-gel method and hydrothermally synthesized HT- TiO_2 samples with different amounts of NH_4F after calcination at 823 K (a–d) and 923 K (e–h)

Fig. 2 H_2O adsorption of the HT- TiO_2 samples calcined at 823 K

Figure 3 shows the UV-vis absorption spectra of the HT- TiO_2 catalysts. While the HT- $\text{TiO}_2(0)$ catalyst exhibit similar absorption edges to that of the pure anatase TiO_2 , the HT- $\text{TiO}_2(0.25)$ and HT- $\text{TiO}_2(1)$ catalysts show a shift to the visible-light range (>430 nm) in the absorption band. This observation indicates that the synthesis in the presence of NH_4F clearly influenced the light absorption characteristics of HT- TiO_2 catalysts. It has been reported that F^- ion doping does not cause a shift in the fundamental absorption edge of TiO_2 with the theoretical band calculations for F^- ion doped TiO_2 [9]. Although we could not detect the

Fig. 3 UV-vis spectra of: **a** HT-TiO₂(0), **b** HT-TiO₂(0.25), and **c** HT-TiO₂(1)

nitrogen atoms by the XPS analysis, an extremely small amount of N contamination from NH₄F in the HT-TiO₂(0.25) and HT-TiO₂(1) catalysts may make the band edges shift to the longer wavelength.

The photocatalytic reactivity for the degradation of iso-butanol diluted in water was investigated on HT-TiO₂ catalysts and the time profiles of the reactions are shown in Fig. 4. The HT-TiO₂(0.25) catalyst exhibits the highest photocatalytic reactivity under UV-light irradiation among the catalysts and also exhibits reactivity for the degradation of 2-propanol, even under visible-light irradiation, as shown in Fig. 5. In the case of HT-TiO₂(0.25), high crystallinity of the anatase phase, the hydrophobic surface property, and the photo absorption ability in the wider range are factors for the high activity. On the other hand, HT-TiO₂(1) exhibits an apparent decrease in photocatalytic activity. Excessive F⁻ doping in HT-TiO₂(1) may play a negative role in photocatalysis, because such sites lead the charge recombination in bulk, which causes the lower photocatalytic activity.

Fig. 4 Photocatalytic degradation of *i*-BuOH diluted in water on HT-TiO₂(0) (●), HT-TiO₂(0.25) (■), and HT-TiO₂(1) (▲)

Fig. 5 Photocatalytic degradation of 2-PrOH diluted in water on HT-TiO₂(0.25) under visible-light irradiation ($\lambda > 430$ nm)

Conclusions

TiO₂ photocatalysts (HT-TiO₂) were synthesized by a hydrothermal method from tetraisopropyl orthotitanate (TPOT) in the presence of NH₄F with different NH₄F/Ti molar ratios. The formation of the well-crystallized anatase phase of TiO₂ and the suppression of phase transition to rutile were observed, even at high calcination temperatures. The photocatalytic activities were apparently affected by the crystallinity of TiO₂ phase, depending on the amount of employed NH₄F. The HT-TiO₂ catalyst with high F⁻ ion content exhibited absorption in the range of visible light. The HT-TiO₂ catalysts synthesized with a moderate amount of NH₄F exhibited efficient photocatalytic activity for the degradation of alcohol diluted in water under both UV-light and visible-light irradiation.

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