Hydrothermal synthesis of visible light sensitive vanadium doped TiO$_2$ photocatalysts and their applications for the degradation of isobutanol diluted in water

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Abstract. Vanadium doped TiO$_2$ photocatalysts (V/TiO$_2$) were synthesized by sol-gel method and hydrothermal treatment using tetraisopropyl orthotitanate (TPOT) and vanadium acetylacetonate in the presence and absence of NH$_4$F. In comparison to the vanadium non-doped TiO$_2$ (pure TiO$_2$), V/TiO$_2$ exhibited the long-tailed absorption in the visible light region above 380 nm. Degradation of isobutanol diluted in water proceeded efficiently on V/TiO$_2$ even under visible light ($\lambda > 430$ nm) irradiation, although pure TiO$_2$ did not show any photocatalytic activities. It was also found that the hydrothermally synthesized V/TiO$_2$ (HT-V/TiO$_2$) in the presence of NH$_4$F possessed high crystallinity of anatase phase and hydrophobic surface, showing the higher photocatalytic activities as compared to those of sol-gel V/TiO$_2$ as well as HT-V/TiO$_2$ prepared in the absence of NH$_4$F.

1. Introduction

In a few decades, various kinds of photocatalysts have been widely investigated for applications in air and water purification as well as the production of clean energy resources [1]. Especially, the photocatalytic degradation of organic pollutants diluted in water is of vital interest to practical utilizations. Among them, titanium dioxide (TiO$_2$) has attracted much attention due to its strong oxidation ability, nontoxicity and low cost, however, TiO$_2$ only show the fascinating photocatalytic properties under UV light irradiation, which limited the use of natural solar light below 3 %. Therefore, the development of TiO$_2$, which can work not only under UV but also visible light, has become one of the most interesting topics for design of efficient and environmentally friendly photocatalytic reaction systems. Along these lines, a number of research groups have attempted to create a bathochromic shift of band gap energy by doping of transition metals into TiO$_2$ [2]. Moreover, Asahi et al. demonstrated that the doping of nitrogen into TiO$_2$ attained the formation of visible light sensitive TiO$_2$ due to the narrowing the band gap [3].

On the other hand, our research has already shown that the surface hydrophobic modification of TiO$_2$ as well as catalysis supports such as zeolite and mesoporous materials by using fluorine led to the enhancement of the adsorption of organic compounds from aqueous solutions and gas phase [4,5].

In the present study, we designed vanadium doped TiO$_2$ photocatalyst (V/TiO$_2$) in the presence and absence of NH$_4$F by a sol-gel method as well as a hydrothermal treatment, aiming at the development of multifunctional materials showing high photocatalytic activity even under visible light irradiation.
The photocatalytic activities were estimated by the degradation of isobutanol diluted in water. In particular, the influences of the preparation methods, the amounts of doping vanadium species as well as the addition of NH₄F on the photocatalytic activities have been examined in detail.

2. Experimental

Tetraisopropyl orthotitanate (TPOT: Ti(OC₃H₇)₄), vanadium acetylacetonate (V(CH₃COCHCOCH₃)₃), ethanol and NH₄F were used as received. The starting solutions were prepared by the addition of NH₄F in H₂O to the mixed TPOT-V(CH₃COCHCOCH₃)₃-ethanol solutions. The molar ratio of starting solutions were as follows; Ti : H₂O : C₂H₅OH : NH₄F : V = 1 : 5 : 5 : 0.05 : X (X = 0, 0.002, 0.01, 0.02). The hydrothermal syntheses of V/TiO₂ (denoted as HT-V/TiO₂(X)) were performed using conventional autoclave. The starting mixture was transferred into an autoclave and kept at 433 K for 48 h. In the case of sol-gel V/TiO₂, above starting mixture was stirred at 298 K for 24 h and then washing in water at 353 K for 24 h. After centrifugation, washing and drying, both types of samples were calcined at 823 K for 5 h.

X-ray diffraction of all samples was measured by Rigaku RINT2500 diffractometer with Cu Kα radiation (λ = 1.5406 Å). The UV-vis absorption spectra were recorded with Shimadzu UV-2200A spectrophotometer.

The photocatalytic activity of samples was evaluated by the degradation of isobutanol diluted in water. The fixed amount of catalysts (50 mg) was dispersed in 25 ml of isobutanol solution (2.61 mmol/L). After stirring under dark conditions for 30 min, the solution was bubbled by oxygen for another 30 min. Then visible light irradiation (λ > 430 nm) was carried out using 500 W Xe-lamp and colored filters (HOYA; L-43). The progress of the reactions was monitored by gas chromatography analysis (GC-14B, Shimadzu). Water adsorption isotherms of the catalysts were measured at 293 K using a conventional vacuum system.

3. Results and discussions

Figure 1 shows the XRD patterns of HT-V/TiO₂ with different contents of vanadium and sol-gel TiO₂ after calcinations at 823 K. All samples only showed the diffraction peaks due to the presence of TiO₂ anatase phase, suggesting that vanadium oxide species were highly dispersed within TiO₂ without the formation of large vanadium oxide clusters under the hydrothermal treatment. The formation of vanadium oxide clusters was also hardly observed in the case of sol-gel V/TiO₂ (data not shown). The intense diffraction peak assigned to the (101) reflection of TiO₂ anatase phase was decreased with increasing of vanadium contents (Fig. 1(b-e)), however, the peak intensity of HT-
V/TiO$_2$ was high as compared to that of sol-gel TiO$_2$ (Fig. 1(a)), indicating that the highly crystalline V/TiO$_2$ was successfully synthesized by the hydrothermal treatment. Moreover, the BET surface areas of HT-V/TiO$_2$ were almost same in the series of samples (ca. 50 m$^2$/g), which was larger than that of sol-gel TiO$_2$ (36 m$^2$/g). By applying the Scherrer’s equation for (101) reflection of TiO$_2$ anatase phase, the crystalline size of HT-V/TiO$_2$ could be determined to be 19 nm (HT-V/TiO$_2$(0)), 21 nm (HT-V/TiO$_2$(0.002)), 18 nm (HT-V/TiO$_2$(0.01)) and 19 nm (HT-V/TiO$_2$(0.02)), respectively. The crystalline sizes were hardly affected by the contents of vanadium oxide species.

Figure 2 shows the UV-vis spectra of HT-V/TiO$_2$ and the commercially available TiO$_2$ (ST-01, anatase). The absorption edge of vanadium non-doped TiO$_2$ (HT-V/TiO$_2$(0)) and ST-01 (Fig. 2(a,e)) was located in the bad gap position of anatase TiO$_2$ at around 380 nm (3.2 eV), which was good coincidence with the results of XRD investigations. On the other hand, as shown in Fig. 2(b-d), vanadium doped TiO$_2$ (HT-V/TiO$_2$(0.002, 0.01, 0.02)) exhibited the new long-tailed absorption in the visible light region above 380 nm, which increases with increasing the amounts of vanadium oxide species. This visible light absorption can be ascribed to the formation of the impurity energy level within the band gap of TiO$_2$. The same phenomena were also observed in the case of sol-gel V/TiO$_2$ (data not shown).

According to the above characterizations, highly crystalline visible light sensitive HT-V/TiO$_2$ can be expected to show high photocatalytic activities even under visible light irradiation as compared to those of sol-gel V/TiO$_2$. Therefore, the reaction rates for the photocatalytic degradation of isobutanol diluted in water were investigated under visible light (λ > 430 nm), aiming at the applications for environmentally friendly photocatalytic reaction systems. As shown in Fig. 3, HT-V/TiO$_2$(0) did not show any photocatalytic activities, however, the degradation of isobutanol was proceeded on HT-V/TiO$_2$(0.002, 0.01, 0.02) even under visible light irradiation. The reaction rate increased upon an increase in the contents of vanadium species while passing through a maximum (HT-V/TiO$_2$(0.01)) and then drastically decreasing in the region of the higher vanadium contents. These results suggested that the reaction rate was effectively improved by the small amounts of vanadium doping into TiO$_2$. It was also found that the reaction rate on HT-V/TiO$_2$(0.01) was about 2.4 times larger than that on sol-gel V/TiO$_2$(0.01), indicating that the large surface area as well as the high crystallinity of the anatase phase were important factors for the preparation of highly functional TiO$_2$ photocatalyst.

Furthermore, the effect of the addition of NH$_4$F into starting solutions for the hydrothermal treatment on the photocatalytic activities was evaluated by the degradation of aqueous isobutanol. The addition of NH$_4$F in the starting solutions led to the formation of highly crystalline TiO$_2$. Moreover, as shown in Fig. 4, the comparative study using HT-V/TiO$_2$(0.01) prepared in the absence and
presence of NH$_4$F (F = 0.0, 0.05) revealed that HT-V/TiO$_2$(0.01)(F = 0.05), which possessed high crystallinity of TiO$_2$ phase, showed the higher photocatalytic activity than that on HT-V/TiO$_2$(0.01)(F = 0.0) under visible light. On the other hand, the amount of adsorbed water on HT-V/TiO$_2$(0.01)(F = 0.05) was much smaller than that on HT-V/TiO$_2$(0.01)(F = 0.0). Thus, the less hydrophilic surface will enhance the transfer of organics from water to catalysis surface, which also led to the higher photocatalytic activities of HT-V/TiO$_2$(0.01)(F = 0.05). A more detailed study of the mechanisms behind these photocatalytic reactions is now underway.

4. Conclusions
In conclusion, vanadium doped TiO$_2$, which exhibited the photocatalytic activities even under visible light irradiation, were successfully synthesized by the hydrothermal treatment with high crystallinity and large surface area. The reaction rate for the degradation of isobutanol on HT-V/TiO$_2$(0.01) exhibited about 2.4 times larger that on sol-gel V/TiO$_2$(0.01), showing that the high crystallinity of TiO$_2$ phase as well as the large surface area plays an important role in this reaction. Moreover, it was found that the addition of NH$_4$F in the starting solutions led to the formation of hydrophobically modified V/TiO$_2$(HT-V/TiO$_2$(0.01)(F = 0.05)), which exhibited the higher photocatalytic activity as compared to that on HT-V/TiO$_2$(0.01) prepared in the absence of NH$_4$F.

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