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Preparation of efficient titanium oxide photocatalysts by an ionized cluster beam (ICB) method and their photocatalytic reactivities for the purification of water

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Abstract

Using an ionized cluster beam (ICB) method, titanium oxide photocatalysts were prepared on porous Vycor silica glass (PVG) and activated carbon fibers (ACF), and their photocatalytic reactivities for the degradation of 2-propanol diluted in water was investigated. Characterizations of these catalysts by means of SEM, XAFS, XRD, XPS and UV–Vis absorption techniques showed that the titanium oxide in transparent thin films could be formed on PVG and titanium oxide clusters could be deposited on the ACF. UV irradiation of these catalysts in a diluted aqueous solution of 2-propanol or 1,2-dichloroethane led to the efficient decomposition of these reactants into CO_2, H_2O and HCl. The titanium oxide catalysts prepared on these porous materials exhibited higher photocatalytic reactivities than TiO_2 powder and titanium oxide catalysts prepared by a conventional impregnation method. The present results have clearly shown that the ICB method is useful in the preparation of titanium oxide photocatalysts combined with porous supports such as PVG and ACF.

Keywords: Ionized cluster beam method; Photocatalyst; Titanium oxide; Purification of water; Activated carbon fiber; Porous silica glass

1. Introduction

The design and development of highly efficient photocatalytic systems which work in the reduction of global air and water pollution has attracted a great deal of attention for their potential in addressing environmental concerns [1–11]. The photocatalytic degradation of various toxic compounds diluted in aqueous solutions using UV irradiated small TiO_2 powder photocatalysts has been widely studied [1,5–9]. However, small TiO_2 powder photocatalysts have to be removed from the degraded solution by centrifugation and filtration after the photodecomposition of the substrates. The design of titanium oxide photocatalysts anchored or embedded onto support materials with large surface areas which could condense dilute polluted substances would be of great significance, not only to avoid the filtration and suspension of small photocatalyst particles, but in order to obtain higher efficiency [11–16]. Recently, the photocatalytic degradation of

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organic compounds has been carried out with TiO_2 thin films prepared by a pasting procedure [17,18], a sol–gel method [19,20], and a Ti-firing technique [21]. Although the sol–gel method is the most popular in preparing these TiO_2 thin film photocatalysts [11,20], it is a wet process and requires the use of solvents and calcination treatments at high temperatures. During calcination at high temperatures, the porous supports, such as activated carbon, usually incur serious damage to their surface porous structure [22–26].

However, the ionized cluster beam (ICB) method applied in the present study is one of the most effective and applicable techniques [27] in preparing such active titanium oxides on support materials under mild and dry conditions [4,14,28,29]. The advantages of using the ICB method are: (1) contamination with various impurities can be easily prevented since the processes are performed in a high vacuum chamber; (2) highly crystalline TiO_2 films can be prepared without any calcination at high temperatures; (3) the various properties of the thin films such as thickness can be controlled while various substrates can also be applied. With these benefits, highly crystalline TiO_2 thin films can be prepared without any structure damaging calcination at high temperatures on the various supports, even on carbon materials which are unstable at high temperatures under air.

In the present study, we deal with the preparation and characterization of titanium oxide thin films prepared on transparent porous silica glass (PVG) and titanium oxide clusters highly dispersed on activated carbon fiber (ACF) using the ICB method. The successful utilization of these photocatalysts for the purification of water have been demonstrated by investigations on their photocatalytic properties and reactivity of these catalysts for the degradation of 2-propanol or 1,2-dichloroethane diluted in water.

2. Experimental

Titanium oxide catalysts loaded on plate ($10 \times 8 \times 1\,mm^3$, ~200 mg) of PVG (Corning, Code 7930, surface area $250\,m^2/g$) and felt ($20 \times 30 \times 5\,mm^3$, ~70 mg) of ACF (Toho Rayon, FX-300, $900\,m^2/g$) were prepared by the ICB method using a Ti metal as the source material under a dilute O_2 atmosphere. A systematic diagram of the ICB method is shown in Fig. 1. The

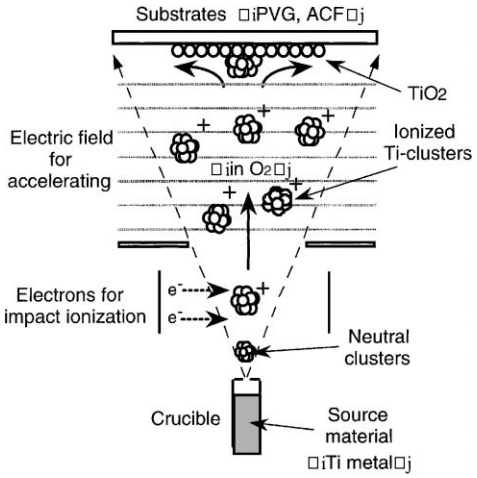

Fig. 1. Systematic diagram of the ICB method.

chamber can be evacuated by a cryo pump to a pressure of 1×10^{-7} torr. High purity Ti metal (99.9%) was used as the source of the titanium oxide. The Ti cluster beam was produced by the ejection of the Ti vapor ionized by the electrons emitted from the ionization filament. The produced ionized clusters were then accelerated by an accelerating electrode. Active titanium oxide thin films were produced by the impingement of the ionized clusters and oxygen gas onto the support substrate. In these experiments, the acceleration voltage, the substrate temperature, and the oxygen gas pressure were 0.25 kV, 523 K, and 2.0×10^{-4} torr, respectively. The loading amount of the titanium oxide was controlled by changing the reaction time.

The photocatalysts were then transferred into a quartz cell containing an aqueous solution of 2-propanol or 1,2-dichloroethane (2.6×10^{-3} mol/l, 25 ml) and irradiated at 295 K using UV light ($\lambda > 280$ nm) from a high-pressure Hg lamp under O_2 atmosphere. The products were analyzed by gas chromatography. Specific photocatalytic reactivities were obtained by the normalization of the initial conversion rates of 2-propanol or 1,2-dichloroethane with the amounts of Ti ions included in the catalysts. The quantum yield for the photocatalytic oxidative disappearance of 2-propanol was defined as the disappeared number of the molecules relative to the number of adsorbed photons by standard potassium ferrioxalate chemical actinometry [14]. The quantum

yields described herein was the average of repeated experiments with about ±10% allowance for error.

The UV–Vis absorption spectra were recorded with a Shimadzu UV 2200A spectrometer at 295 K. The X-ray photoelectron spectroscopy (XPS) spectra were measured at 295 K with a V.G. Scientific ESCASCOPE photoelectron spectrometer using Mg Kα radiation. X-ray diffraction patterns of the catalysts were obtained at 295 K with a Rigaku RAD-γA X-ray diffractometer using Cu Kα radiation. Scanning electron microscopy (SEM) was performed using a Hitachi S-4500 model. The X-ray absorption fine structure (XAFS) spectra, X-ray absorption near edge structure (XANES), and extended X-ray absorption fine structure (EXAFS), were measured at the BL-7C facility of the Photon Factory at the National Laboratory for High-Energy Physics, Tsukuba. The Ti K-edge absorption spectra were recorded in the fluorescence mode at 295 K. The normalized spectra were obtained by a procedure described in previous literature [30] and Fourier transformation was performed on k^3-weighted EXAFS oscillations in the range 3–10 $Å^{-1}$.

3. Results and discussion

3.1. TiO_2 thin films embedded on PVG

Transparent titanium oxide thin films of various thicknesses were prepared on PVG by the ICB method. Fig. 2 shows the XANES and FT-EXAFS spectra of the TiO_2/PVG catalysts having a 20 nm thickness of TiO_2. Three small well-defined pre-edge peaks could be observed in the XANES spectra and an intense peak attributed to the neighboring titanium atoms (Ti–O–Ti) appears in the FT-EXAFS spectra. These spectra features are very similar to those of anatase TiO_2 crystals [30], indicating anatase crystals were formed even in the thin film. As shown in Fig. 3, the bands assignable to anatase phase were observed as main phase with weak bands for rutile phase in the XRD patterns of TiO_2/PVG catalysts. With an increase in the thickness of the film, the intensity of these bands increased. These results of XRD and XAFS results show that titanium oxide thin films prepared under the present conditions exist mainly in anatase structure.

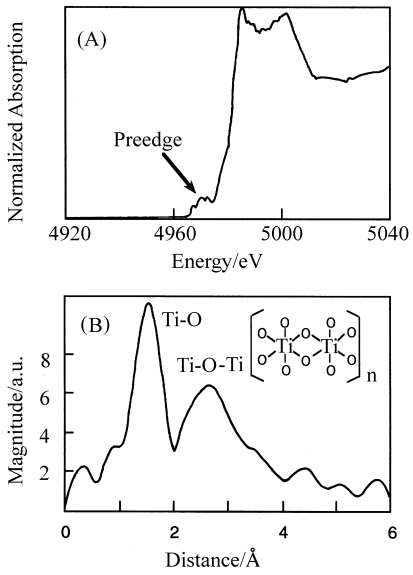

Fig. 2. The XANES (A) and FT-EXAFS (B) spectra of TiO_2/PVG photocatalysts with film thickness of 20 nm prepared by the ICB method (calcination: 723 K under air for 5 h).

The O(1s) photoelectron transition for TiO_2/PVG catalysts was measured by XPS spectroscopy and the spectra obtained with the catalysts having various film thicknesses are shown in Fig. 4, as well as those of pure SiO_2 and TiO_2 powders. The binding energies of the O(1s) bands in the XPS spectra of the SiO_2 and TiO_2 powders were 534.5 and 529.5 eV, respectively. The TiO_2/PVG catalysts exhibited a main band at around 529.5 eV with a shoulder at around 534.5 eV

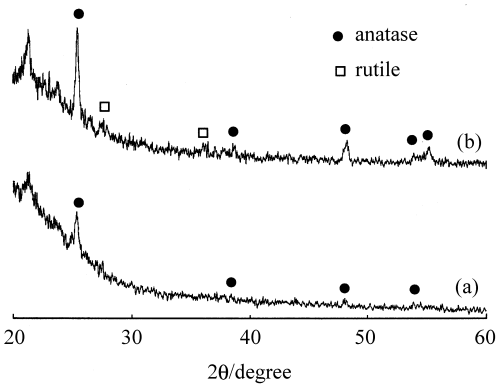

Fig. 3. The XRD patterns of TiO_2/PVG photocatalysts with film thickness of: (a) 100 and (b) 300 nm prepared by the ICB method.

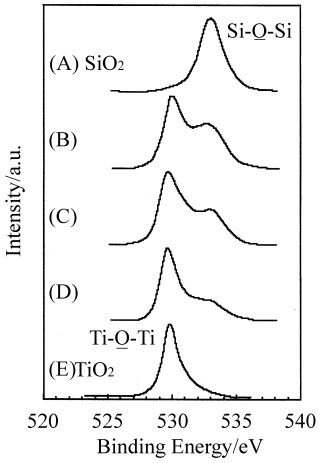

Fig. 4. The X-ray photoelectron spectra of the O(1s) level for (A) SiO_2, (E) TiO_2 powder and (B–D) TiO_2/PVG photocatalysts having various film thicknesses prepared by the ICB method. The film thickness: (B) 2, (C) 100, (D) 300 nm (calcination: 723 K under air for 5 h).

which can be assigned to the oxygen atoms in TiO_2 and SiO_2 phases, respectively. With an increase in the film thickness, the intensity of the band at 529.5 eV increased and that of the shoulder at 534.5 eV decreased, indicating that the covering of the porous glass support with the TiO_2 film was completed.

The transmittance spectra of the TiO_2 thin films in the UV–Vis wavelength region are shown in Fig. 5.

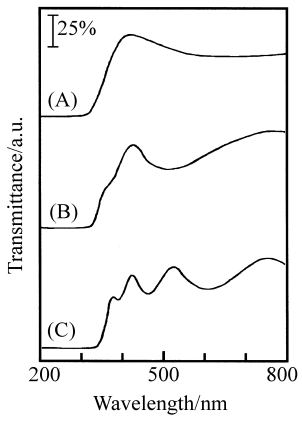

Fig. 5. The transmittance spectra of TiO_2/PVG photocatalysts having various film thicknesses prepared by the ICB method. The film thickness: (A) 50, (B) 100, (C) 300 nm (calcination: 723 K under air for 5 h).

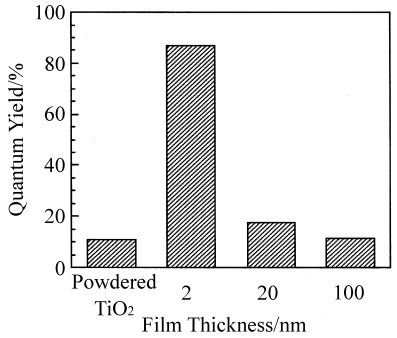

Fig. 6. The photocatalytic reactivity of TiO_2/PVG photocatalysts having various film thickness prepared by the ICB method and powdered TiO_2 for the photocatalytic degradation of 2-propanol diluted in water (calcination: 723 K under air for 5 h).

In these spectra, TiO_2 thin films having a thickness larger than 100 nm clearly show specific interference fringes, indicating that transparent and uniform TiO_2 thin films are formed in these catalysts. As the film thickness becomes smaller, the absorption of the TiO_2 thin films were found to shift toward shorter wavelength regions. This can be attributed to the quantum size effect of the thin films caused by the presence of small TiO_2 particles which compose the transparent TiO_2 thin films.

UV irradiation of the catalysts suspended in an aqueous solution of 2-propanol at 295 K under an O_2 atmosphere led to the formation of acetone and CO_2. Acetone was further decomposed into CO_2 under prolonged irradiation [14,15]. As shown in Fig. 6, the quantum yields of the photocatalytic degradation of 2-propanol using these titanium oxide thin films were higher than the yields of standard TiO_2 photocatalyst (P-25). Fig. 6 also shows the effect of the TiO_2 film thickness on the photocatalytic reactivity of the thin film photocatalysts. The photocatalytic reactivity of these TiO_2 thin films are strongly dependent on the film thickness, i.e., the thinner the films, the higher the reactivity. Moreover, the quantum size effect of the thinner films observed by absorption measurement seems to be responsible to the increase in photocatalytic efficiency. These results clearly indicate that the ICB method can be applied to prepare highly reactive transparent TiO_2 thin film photocatalysts.

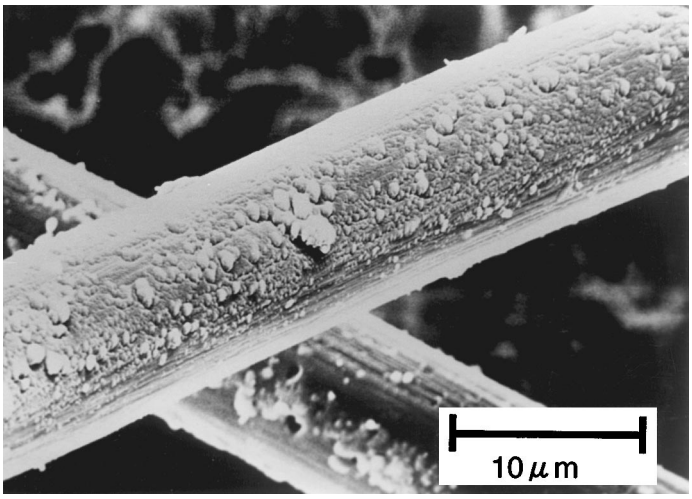

Fig. 7. The SEM image of TiO_2/ACF photocatalyst prepared by the ICB method (Ti content: 3 wt.%, calcination: 523 K under air for 5 h).

3.2. Clustered TiO_2 embedded on ACF

Characterizations of TiO_2/ACF photocatalysts prepared by the ICB method by the SEM technique showed the titanium oxides to be deposited on the ACF as small clusters (Fig. 7). The migration of the titanium ion clusters was not easy on ACF with its numerous micropores, resulting in the formation of titanium oxide clusters and not thin films [14,28]. XRD and XAFS measurements of the TiO_2/ACF photocatalysts suggest crystalline anatase as the main structure present.

Fig. 8 shows the reaction time profiles of the liquid-phase photocatalytic reaction on the TiO_2/ACF photocatalysts. In the initial stage of the reaction under dark conditions, the adsorption of 1,2-dichloroethane onto the photocatalysts can be observed. This process followed the Langmuir adsorption and the adsorption was saturated within 1 h before the UV irradiation. When UV light is turned on, the 1,2-dichloroethane decomposes into CO_2, H_2O and HCl. As an intermediate species, small amount of vinyl chloride was appeared and subsequently disappeared. As shown in Figs. 8 and 9, these TiO_2/ACF photocatalysts exhibit higher photocatalytic reactivity than the catalysts prepared on ACF by the impregnation method using an aqueous solution of $(NH_4)_2TiO(C_2O_4)_2$. In the preparation of TiO_2 catalyst using conventional chemical procedures such as the impregnation method, calcination at high temperatures is required to obtain highly crystalline TiO_2 catalyst and during this calcination process, the ACF undergoes a serious structural damage, losing its adsorption abilities. The present results indicate that with the ICB method it is possible to prepare highly crystalline anatase titanium oxide photocatalysts at low calcination temperatures without damaging the microporous structure and adsorption properties of the ACF supports.

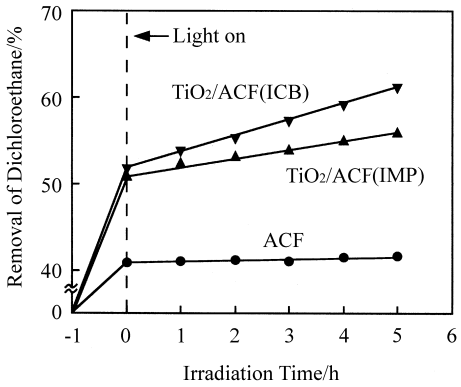

Fig. 8. The reaction time profiles of the photocatalytic degradation of 1,2-dichloroethane diluted in water on the TiO_2/ACF photocatalysts prepared by the ICB method and the impregnation method using an aqueous solution of $(NH_4)_2TiO(C_2O_4)_2$ (Ti content: 3 wt.%, calcination: 523 K under air for 5 h).

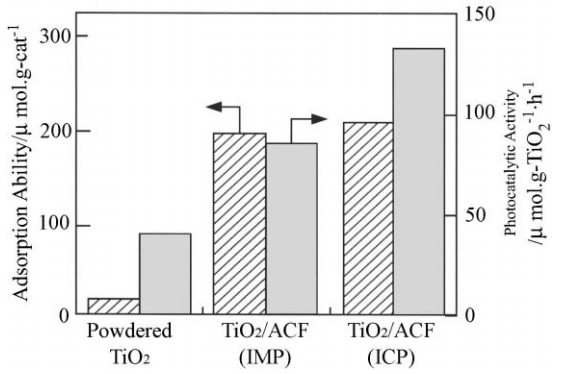

Fig. 9. The adsorption abilities and photocatalytic reactivities for the degradation of 1,2-dichloroethane diluted in water on the standard powdered TiO_2 (P-25) and the TiO_2/ACF photocatalysts prepared by the ICB method and the impregnation method using an aqueous solution of $(NH_4)_2TiO(C_2O_4)_2$ (Ti content: 3 wt.%, calcination: 523 K under air for 5 h).

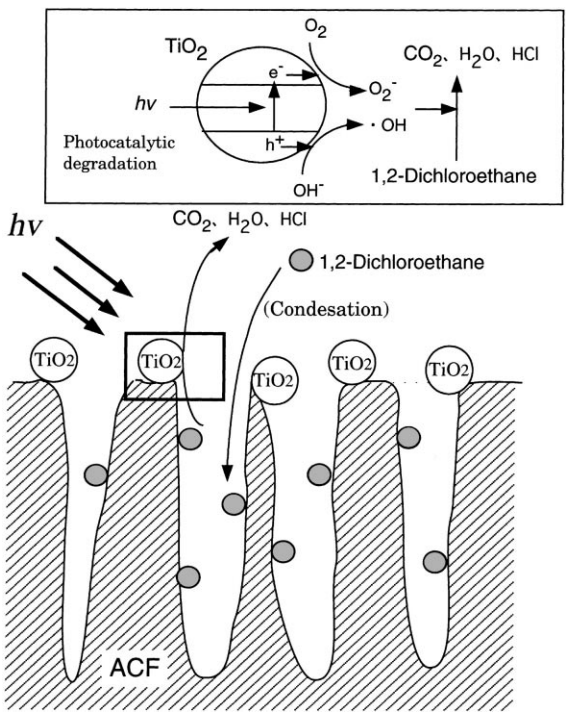

Fig. 10. Scheme for the adsorption and photocatalytic degradation of 1,2-dichloroethane diluted in water on the TiO_2/ACF photocatalyst prepared by the ICB method.

Fig. 9 also shows that the adsorption and photocatalytic properties of standard powdered TiO_2 (P-25) and TiO_2/ACF photocatalysts. The TiO_2/ACF photocatalyst prepared by the ICB method with ACF having a larger surface area exhibits a higher adsorption ability and photocatalytic reactivity than standard powdered TiO_2 photocatalyst (P-25). These results indicate that combining the superior adsorption properties of ACF and the efficient photocatalytic reactivity of TiO_2 clusters allows the efficient degradation of 1,2-dichloroethane diluted in water (Fig. 10).

4. Conclusions

Unique TiO_2 photocatalysts loaded on PVG or on ACF by means of a combination of the ICB method and calcination at a relatively low temperature, were developed for various significant photocatalytic reactions especially for the purification of water. These TiO_2 photocatalysts had an anatase phase as the main structure and were found to exhibit highly efficient photocatalytic reactivity. The crystalline structure and electronic state of the TiO_2 thin films supported on PVG varied with the film thickness and affected the reactivity of the TiO_2 thin film photocatalyst; the thinner the TiO_2 films, the higher the photocatalytic reactivity. In the case of TiO_2/ACF, the ACF remained intact even with the preparation of the TiO_2 photocatalysts on carbon fibers at low calcination temperatures, showing a high condensation effect and high photocatalytic reactivity.

Acknowledgements

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