Degradation of propanol diluted in water under visible light irradiation using metal ion-implanted titanium dioxide photocatalysts

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Abstract

The metal ion-implantation of titanium dioxide (TiO_2) with metal ions (V^+, Mn^+, Fe^+) at high energy acceleration and the subsequent calcination of these metal ion-implanted TiO_2 in oxygen at around 725 K resulted in a definite shift in the absorption spectra toward visible light regions. These catalysts exhibited photocatalytic reactivity for degradation of 2-propanol diluted in water under visible light irradiation ($\lambda > 450$ nm). XAFS studies have revealed that the implanted metal ions are located at the lattice positions of Ti^{4+} in TiO_2 after the calcination. These spectroscopic studies show that the substitution of Ti ions in TiO_2 lattice with implanted metal ions is important to modify TiO_2 to be able to adsorb visible light and operate as photocatalysts under visible light irradiation. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The photocatalytic degradation of various toxic compounds diluted in aqueous solutions using UV irradiated TiO_2 photocatalysts has been widely studied [1–10]. However, TiO_2 catalysts cannot absorb visible light and only make use of 3–5% of the solar beam that can reach the earth, necessitating the utilization of an ultraviolet light source. It is, therefore, necessary to develop a photocatalytic system which can be applied under visible and/or solar light irradiation [11–13].

The metal ion-implantation using the accelerated metal ion beam has been developed to modify the electronic structure of semiconductoring electronic materials [14,15]. The metal ions are accelerated in the electronic field and injected to the sample target as the ion beam. These metal ions can have the interaction in the different manner with the sample surface depending on their kinetic energy. In the metal ion-implantation, metal ions are accelerated enough to have the high kinetic energy (50–200 keV) and can be implanted into the bulk of samples. Although the well-defined semiconductor electronic materials have been developed with these unique properties of the ion beam techniques, their appli-

cations to the preparation of catalysts and/or photocatalysts have rarely been made yet [11,16–18].

In the present study, the application of metal ion-implantation method has been made to improve the electronic properties of TiO_2 photocatalysts to realize the utilization of visible light. The photocatalytic properties of these unique TiO_2 photocatalysts for the degradation of 2-propanol diluted in water under visible light irradiation have been investigated as a model reaction of the photocatalytic purification of water using solar light. The local structures of metal ions implanted in TiO_2 have been analyzed by XAFS measurement to understand the mechanism of these unique performance.

2. Experimental details

The TiO_2 powder photocatalyst was prepared by a sol–gel method from ethanol solution (50 vol.%) of titaniumisopropoxide supplied by Kishida Chemicals, Japan, and calcined at 723 K for 5 h under air. The surface are of the TiO_2 photocatalyst was 58 m²/g and the XRD analysis indicated that the TiO_2 photocatalyst has only anatase crystalline phase with 10.2 nm crystallite size. The TiO_2 photocatalyst (100 mg) was pressed into a wafer of 13 mm diameter and 1 mm thickness. The catalyst was heated in O_2 at 723 K for

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5 h before use, then placed in a quartz cell with an aqueous solution of 2-propanol (2.6×10^{-3} mol/l, 25 ml) and irradiated at 295 K using visible light ($\lambda > 450$ nm) from a 100 W high-pressure Hg lamp with a colored filter under O_2 atmosphere in the system. The reaction products were analyzed by gas chromatography. The diffuse reflectance UV–VIS spectra of the catalysts were measured using a Shimadzu UV-2200 A spectrophotometer at 295 K. The depth profile of metal ions implanted into TiO_2 wafer photocatalyst was obtained measuring the SIMS spectra using the ADEPT1010 instrument of Physical Electronics. The V K-edge XAFS spectra were obtained in the fluorescence mode at 295 K at the BL-9A facility [19] of the Photon Factory at the National Laboratory for High Energy Physics (KEF-PF) in Tsukuba with a ring energy of 2.5 GeV. The Fe K-edge XAFS spectra were obtained in the fluorescence mode at 295 K at the BL-01B1 facility of the SPring-8 in Kouto with a ring energy of 8 GeV. The normalized spectra were obtained by a procedure described in previous literature [20], and Fourier transformations were performed on $k3$-weighted EXAFS oscillations in the range of 3–14 Å^{-1}.

3. Results and discussion

The TiO_2 (anatase) photocatalyst prepared by the sol–gel method and calcination can absorb only UV light shorter than about 390 nm and cannot absorb visible light, as shown in Fig. 1. As shown in Fig. 1, the absorption band of the TiO_2 implanted with V ions by the ion-implantation with high acceleration energy (150 keV) and calcined in O_2 at 725 K after ion-implantation has been found to shift to visible light regions, the extent depending on the amount of V ions implanted. The TiO_2 implanted with V ions of 13.2–22.0×10^{-7} mol/g-cat. can absorb the visible light even at around 600–650 nm. The V ions implanted within the bulk of TiO_2 can modify the electronic properties of the TiO_2 surface layer. As shown in Fig. 2, the ion-implantation with the other

Fig. 2. The diffuse reflectance UV–VIS spectra of TiO_2 (a) and TiO_2 implanted with V (b), Mn (c), and Fe (d) ions photocatalysts. Ion acceleration energy: 150 keV. Amounts of implanted metal ions: 13.2×10^{-7} mol/g-cat.

transition metal ions such as Cr, Mn, Fe, Co, Ni, Cu, etc. are also effective to modify the properties of TiO_2 to make a large shift in the absorption band to the visible light region. On the other hand, ion-implantation with ions such as Ti, Ar, Na, etc. is not effective at all to modify the properties of TiO_2 to make a shift of absorption band to the longer wavelength region.

Fig. 3 shows the depth concentration profiles of V ions obtained from SIMS measurements with the V-implanted TiO_2 wafer where ion-implantation was performed at 150 keV with the different amount of implanted ions; 2.2–22.0×10^{-7} mol/g-cat. The most V ions are implanted within the bulk of TiO_2 wafer photocatalyst but not on the top surface of photocatalyst. The maximum depth concentration of the V ions was found to be about 200 nm (sputtering time of 200 s) in these catalysts. With increase of the amounts of ions implanted, the position of implantation of metal ions is not changed and the only amount of implanted metal ions increased. These detailed SIMS analysis indicate that the V ions are injected up to a depth of about 2000 nm (sputtering time of 2000 s) from the surface and highly dispersed within the TiO_2 wafer photocatalyst, but the deposition on
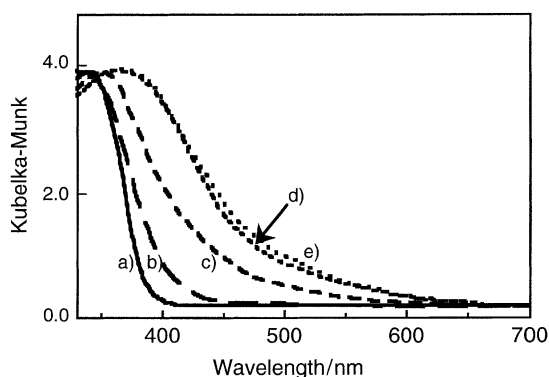
Fig. 1. The diffuse reflectance UV–VIS spectra of TiO_2 (a) and V ion-implanted TiO_2 photocatalysts (b)–(e). Ion acceleration energy: 150 keV. Amounts of implanted V ions ($\times 10^{-7}$ mol/g-cat.): (a) 0; (b) 2.2; (c) 6.6; (d) 13.2; (e) 22.0.
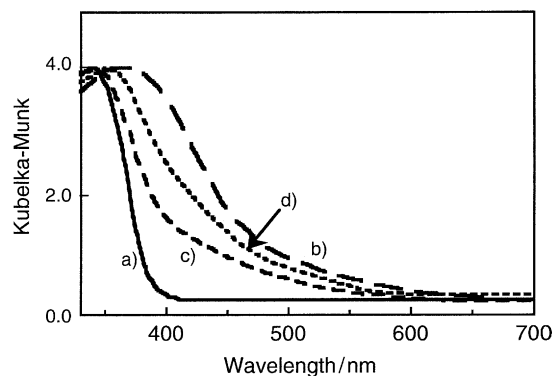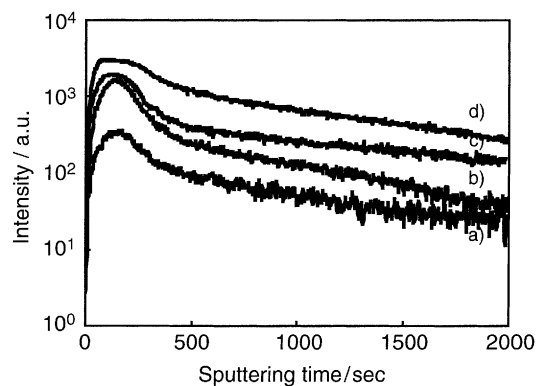
Fig. 3. The depth profiles of V ions content for the V ion-implanted TiO_2 wafer. Ion acceleration energy: 150 keV. Amounts of implanted V ions ($\times 10^{-7}$ mol/g-cat.): (a) 2.2; (b) 6.6; (c) 13.2; (d) 22.0.
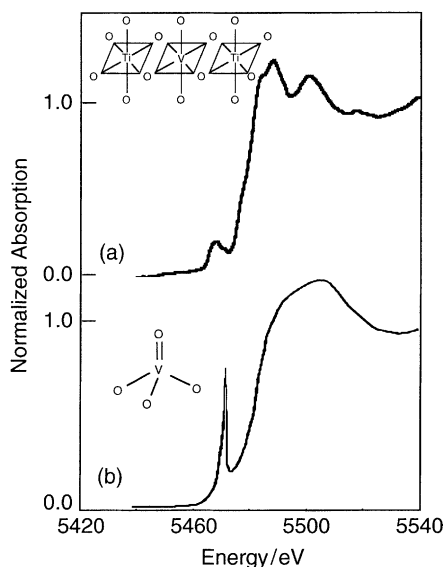
Fig. 4. The V K-edge XANES spectrum of V ion-implanted TiO$_2$ (a) and VO(O–i–Pr)$_3$ (b). Ion acceleration energy: 150 keV. Amounts of implanted V ions: 13.2×10^{-7} mol/g-cat.

Fig. 5. The XANES (left) and Fourier transforms EXAFS (right) spectra of the Fe ion-implanted TiO$_2$ (a, A) and α-Fe$_2$O$_3$ (b, B). Ion acceleration energy: 150 keV. Amounts of implanted Fe ions: 13.2×10^{-7} mol/g-cat.

the top surface is prevented. The same phenomena were also observed previously in the case of metal ion-implantation into TiO$_2$ thin film [18]. Furthermore, XPS measurements of the catalysts did not show any evidence of the presence of V ions on the TiO$_2$ surface indicating that V ions are highly dispersed within the bulk of TiO$_2$ wafer photocatalyst but not on the top surface. Thus, the use of the metal ion-implantation technique to modify the electronic properties of TiO$_2$ photocatalysts without the serious structural destruction of the top surface of the TiO$_2$ photocatalysts can be considered as one of the most significant advantages in the modification of the photocatalyst.

Fig. 4 shows the V K-edge XANES spectrum of V ion-implanted TiO$_2$ photocatalyst. V ion-implanted TiO$_2$ shows a very weak pre-edge peak in its XANES spectrum, while the intense sharp pre-edge peak can be observed with V compounds having four-coordinated or five-coordinated geometry [21]. Considering the observation of this weak pre-edge peak and its peak position, it is found that V ions exist as V^{3+} or V^{4+} ions in octahedral coordination in the lattice position of TiO$_2$. Fig. 5 shows the XANES and Fourier transforms of EXAFS (FT-EXAFS) spectra of the Fe ion-implanted TiO$_2$ photocatalyst. The Fe ion-implanted TiO$_2$ photocatalyst exhibits an XANES spectrum without any intense pre-edge peaks. And in the FT-EXAFS, a peak due to the neighboring titanium atoms in TiO$_2$ lattice (Fe–O–T̲i̲) can be observed as well as a peak due to the neighboring oxygen atoms (Fe–O̲). These peak positions are different from those of α-Fe$_2$O$_3$ (Fe–O–F̲e̲, Fe–O̲), respectively. These results indicate that Fe ions exist as isolated octahedrally coordinated Fe^{3+} species substituted with lattice Ti^{4+} ions in the lattice of TiO$_2$. These results obtained using XAFS technique suggest that the substitu-
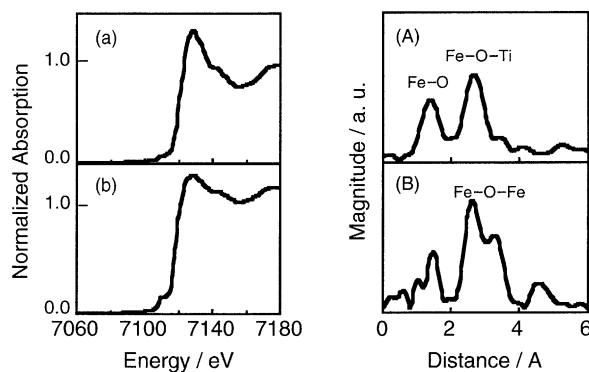
tion of octahedrally coordinated Ti^{4+} ions in TiO$_2$ lattice with implanted metal ions is important to modify TiO$_2$ to be able to adsorb visible light and operate as efficient photocatalyst under visible light irradiation.

In the previous study [18], we have carried out the ab initio molecular orbital calculation on the basis of the density functional theory method to prove this mechanism induced by the metal ion-implantation using the binuclear cluster models with the octahedral coordination similar to the coordination of anatase TiO$_2$. The results of calculations have indicated that in the metal ion-implanted TiO$_2$ the overlap of the conduction band due to Ti(d) of TiO$_2$ and the metal(d) orbital of the implanted metal ions can decrease the band gap of TiO$_2$ to enable to adsorb the visible light. Combined with the results obtained from XAFS analysis and theoretical calculations, it can be proposed that the local coordination geometry realized by the substitution of Ti ions in TiO$_2$ lattice with implanted metal ions is essential to modify TiO$_2$ to be able to adsorb visible light.

As shown in Fig. 6, the visible light irradiation ($\lambda >$ 450 nm) of the V ion-implanted TiO$_2$ in a diluted aqueous solution of 2-propanol under O$_2$ atmosphere led to the formation of acetone and CO$_2$. After prolonged visible light irradiation acetone was finally decomposed into CO$_2$ and H$_2$O. The formation of these products were not detected under dark conditions. The presence of the metal ion-implanted TiO$_2$ as well as visible light irradiation are indispensable for the photocatalytic reaction to take place and the degradation of 2-propanol occurs photocatalytically on the catalyst surface. Under UV light irradiation, the photocatalytic reactivity for the degradation of propanol on the metal ion-implanted TiO$_2$ was similar to the un-implanted original TiO$_2$ photocatalyst, indicating that the implanted metal ions do not work as the electron–hole recombination centers.

Fig. 7 shows the effect of amount of implanted V ions on the specific photocatalytic reactivities on the V ion-implanted TiO$_2$ photocatalysts for the oxidative degradation of 2-propanol diluted in water under visible light

$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[O_2]{H_2O} CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \longrightarrow CO_2 + H_2O$$
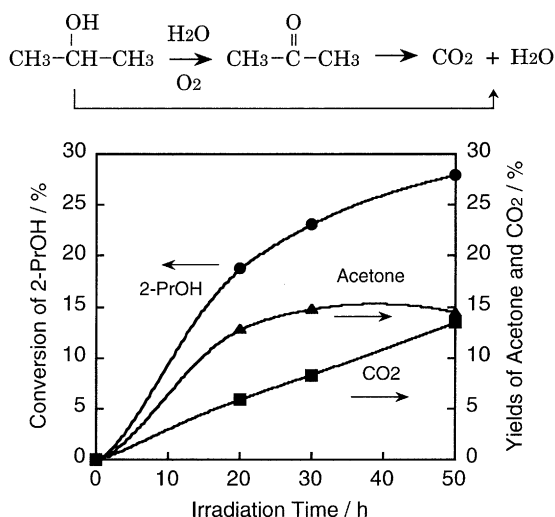

Fig. 6. The reaction time profiles of the photocatalytic oxidative degradation of 2-propanol diluted in water on the V ion-implanted TiO_2 photocatalysts under visible light irradiation ($\lambda > 450$ nm). Ion acceleration energy: 150 keV. Amounts of implanted V ions: 13.2×10^{-7} mol/g-cat.
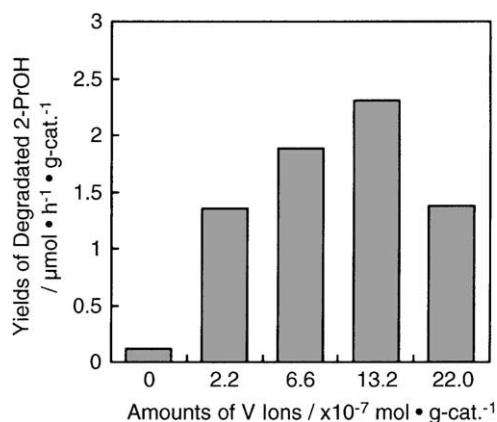

Fig. 7. The effect of the amounts of implanted V ions on the specific photocatalytic reactivities of the V ion-implanted TiO_2 photocatalysts for the oxidative degradation of 2-propanol diluted in water under visible light irradiation ($\lambda > 450$ nm). Amounts of implanted V ions ($\times 10^{-7}$ mol/g-cat.): (a) 2.2; (b) 6.6; (c) 13.2; (d) 22.0.

irradiation ($\lambda > 450$ nm). The photocatalytic degradation of propanol proceeded on the V ion-implanted TiO_2 photocatalytsts, while the reactivity was hardly observed on the un-implanted original TiO_2 photocatalyst. With increase in the amounts of implanted V ions, the photocatalytic reactivity increases constantly and the maximum photocatalytic reactivity is observed on the catalyst with the amount of 13.2×10^{-7} mol/g-cat. implanted V ions. On the other hand, the excess amount of implanted V ions leads to the decrease of the photocatalytic reactivity. As shown in Fig. 1, the absorption bands of the V ion-implanted TiO_2 shift to the longer wavelength region efficiently within the amounts of implanted ions of 13.2×10^{-7} mol/g-cat. This efficient shift of absorption band can realize the increase

of photon numbers which can be absorbed by catalyst and utilized for the photocatalytic reaction. The excess amount of implanted metal ions probably brings about the increase of deposited metal ions which cover the top surface of catalyst and suppress the photocatalytic reaction. These results indicate that the moderate amount of implanted metal ions is suitable for realize the efficient photocatalytic reaction under visible light irradiation.

4. Conclusions

By the metal ion-implantation method, metal ions are accelerated enough to have the high kinetic energy and can be implanted into the bulk of TiO_2 photocatalysts. TiO_2 photocatalysts which can absorb visible light and work as a photocatalyst efficiently under visible light irradiation were successfully prepared using this advanced technique. The UV–VIS absorption spectra of these metal ion-implanted TiO_2 photocatalysts were found to shift toward visible light regions depending on the amount and the kind of metal ions implanted. They were found to exhibit an effective photocatalytic reactivity for the liquid-phase degradation of 2-propanol diluted in water at 275 K under visible light ($\lambda > 450$ nm) irradiation. The investigation using XAFS analysis suggested that the substitution of Ti ions in TiO_2 lattice with implanted metal ions is important to modify TiO_2 to be able to adsorb visible light.

References

[1] D.F. Ollis, H. Al-Ekabi (Eds.), Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam, 1993.
[2] N. Serpone, E. Pelizzetti (Eds.), Photocatalysis, Wiley, New York, 1988.
[3] E. Pelizzetti, M. Schiavello (Eds.), Photochemical Conversion and Storage of Solar Energy, Kluwer Academic Publishers, The Netherlands, 1991.
[4] H. Courbon, P. Pichat, J. Chem. Soc., Faraday Trans. I 80 (1984) 3175.
[5] P.V. Kamat, Chem. Rev. 93 (1993) 267.
[6] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
[7] M.A. Fox, M.T. Dulay, Chem. Rev. 93 (1993) 341.
[8] A. Heller, Acc. Chem. Res. 28 (1995) 503.

[9] M. Anpo, H. Yamashita, in: M. Anpo (Ed.), Surface Photochemistry, Wiley, Chichester, 1996, p. 117.

[10] M. Anpo, H. Yamashita, in: M. Schiavello (Ed.), Heterogeneous Photocatalysis, Wiley, Chichester, 1997, p. 133.

[11] M. Anpo, Y. Ichihashi, M. Takeuchi, H. Yamashita, Stud. Surf. Sci. Catal. 121 (1999) 305.

[12] A. Kudo, M. Sekizawa, Chem. Commun. (2000) 1371.

[13] K. Sayama, H. Arakawa, J. Chem. Soc., Faraday Trans. 93 (1997) 1647.

[14] A.J.T. Holmes, Beam Transport, Gordon and Breach, New York, 1979.

[15] A. Anders (Ed.), Handbook of Plasma Immersion: Ion Implantation and Deposition, Wiley, New York, 2000.

[16] H. Yamashita, M. Harada, Y. Ichihashi, M. Anpo, J. Phys. Chem. B 102 (1998) 10707.

[17] H. Yamashita, Y. Ichihashi, M. Takeuchi, M. Anpo, J. Synchrotron Rad. 6 (1999) 451.

[18] H. Yamashita, M. Harada, J. Misaka, M. Takeuchi, Y. Ichihashi, F. Goto, M. Ishida, T. Sasaki, M. Anpo, J. Synchrotron Rad. 8 (2001) 569.

[19] M. Nomura, A. Koyama, J. Synchrotron Rad. 6 (1999) 182.

[20] H. Yamashita, M. Matsuoka, K. Tsuji, Y. Shioya, M. Anpo, M. Che, J. Phys. Chem. 100 (1996) 397.

[21] S.G. Zhang, S. Higashimoto, H. Yamashita, M. Anpo, J. Phys. Chem. B 102 (1998) 5590.