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Photocatalytic degradation of organic compounds diluted in water using visible light-responsive metal ion-implanted TiO_2 catalysts: Fe ion-implanted TiO_2

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Abstract

The application of metal ion-implantation method has been made to improve the electronic properties of the TiO_2 photocatalyst to realize the utilization of visible light. The photocatalytic properties of these unique TiO_2 photocatalysts for the purification of water have been investigated. By the metal ion-implantation method, metal ions (Fe^+, Mn^+, V^+, etc.) are accelerated enough to have the high kinetic energy (150 keV) and can be implanted into the bulk of TiO_2. 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 295 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.

Keywords: Photocatalyst; TiO_2; Metal ion-implantation; Visible light; Degradation of organic compounds; XAFS

1. Introduction

Photocatalytic degradation of various toxic hazardous organic compounds dissolved in water using TiO_2 photocatalysts has been widely studied [1–9]. Design and development of TiO_2 photocatalysts which operate effectively under visible light or solar beam irradiation are required for a large-scale utilization of TiO_2 photocatalysts. However, TiO_2 photocatalysts 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 [9–14]. In our previous studies, it has been shown that the metal ion-implanted TiO_2 photocatalysts with various transition metals such as V and Cr ions absorb visible light and operate effectively under visible or solar light irradiation for the photocatalytic decomposition of NO into N_2 and O_2 as the gas-phase reaction [9–12]. Although the well-defined semiconductor electronic materials have been developed with these unique properties of the ion-implantation techniques, their applications to the

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preparation of catalysts and/or photocatalysts have rarely been made yet [9–11,15–17].

In the present study, we deal with the preparation and characterization of Fe^+ ion-implanted TiO_2 photocatalysts and the successful utilization of these catalysts for the photocatalytic degradation of 2-propanol diluted in water under visible light irradiation 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 performances. In addition, these catalysts were compared with the TiO_2 modified by the addition of Fe ions using the chemical sol–gel method.

2. Experimental

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 area of the TiO_2 photocatalyst was 58 m^2/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. Metal ions implanted TiO_2 photocatalysts were prepared by the metal ion-implantation method. The implantation of metal ions (Fe^+, Mn^+, V^+, etc.) to TiO_2 was carried out using an ion-implanter (Fig. 1) consisting of a metal ion source, mass analyzer, and high voltage ion accelerator (150 keV). In this method, the metal ions are accelerated in the electronic field and injected to the sample target (TiO_2 wafer) as the ion beam. These metal ions can have the interaction in the different manner with the sample surface depending on their kinetic energy [15]. In the ion-implantation, metal ions are accelerated enough to have the high kinetic energy (150 keV) and can be implanted into the bulk of samples. On the other hand, the TiO_2 chemically doped with Fe was prepared by the sol–gel method from titaniumisopropoxide, acetylacetone Fe(III) and ethanol. The catalyst was heated in O_2 at 723 K for 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-2200A spectrophotometer at 295 K. The Fe K-edge XAFS spectra were obtained in the fluorescence mode at 295 K at the BL01B1 facility of the SPring-8 at the Japan Synchrotron Radiation Research Institute (JASRI) in Ako with a ring energy of 8.0 GeV. The normalized

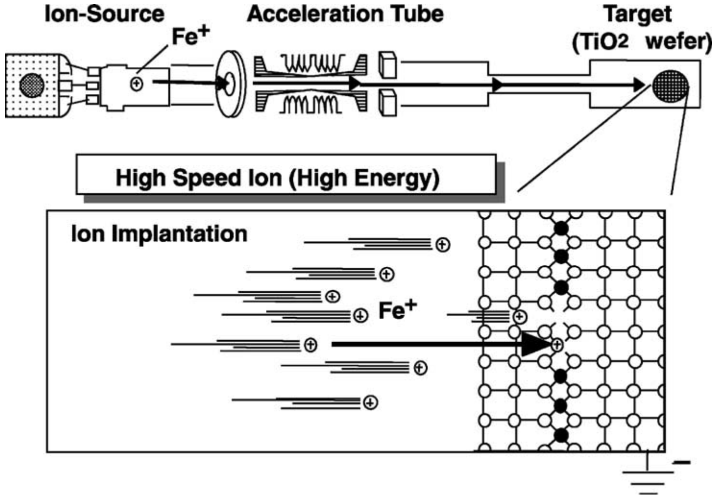

Fig. 1. Systematic diagram of a metal ion (Fe^+)-implantation into TiO_2 wafer samples.

spectra were obtained by a procedure described in previous literature [18], and Fourier transformations were performed on k3-weighted EXAFS oscillations in the range of 3–15 $Å^{-1}$.

3. Results and discussion

The TiO_2 photocatalyst (anatase) prepared by the sol–gel method and calcined can absorb only UV light shorter than about 390 nm and cannot absorb visible light, as shown in Fig. 2. As shown in Fig. 2, the absorption band of the TiO_2 implanted with Fe ions by the ion-implantation with high acceleration energy (150 keV) and calcined in O_2 at 723 K after ion-implantation has been found to shift to visible light regions, the extent depending on the amount of Fe ions implanted. The TiO_2 implanted with Fe ions of (13.2–22.0) × 10^{-7} mol/g_{cat} can absorb the visible light even at around 600 nm. The Fe ions implanted within the bulk of TiO_2 can modify the electronic properties of the TiO_2 surface layer. The ion-implantation with the other transition metal ions such as V, Cr, Mn, Co, Ni, Cu, etc. has been found to be also effective to modify the properties of TiO_2 to make a large shift in the absorption band to the visible light region [9–11]. On the other hand, ion-implantation with ions such as Ti, Ar, Na, etc was not effective at all to modify the properties of TiO_2 to make a shift of absorption band to the longer wavelength region.

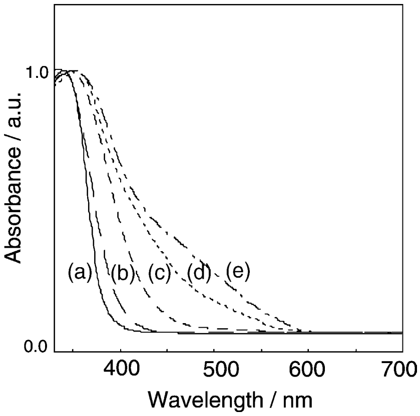

Fig. 2. The diffuse reflectance UV-Vis spectra of TiO_2 (a) and Fe ion-implanted TiO_2 photocatalysts ((b)–(e)). Ion acceleration energy: 150 keV. Amounts of implanted Fe ions (×10^{-7} mol/g_{cat}): (a) 0, (b) 2.2, (c) 6.6, (d) 13.2, and (e) 22.0.

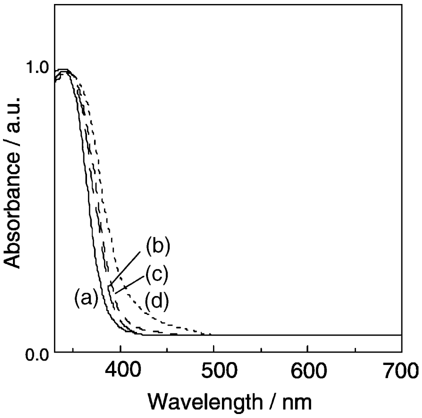

Fig. 3. The diffuse reflectance UV-Vis spectra of TiO_2 (a) and the TiO_2 photocatalysts chemically doped with Fe ions by the sol–gel ((b)–(e)). Ion acceleration energy: 150 keV. Amounts of doped Fe ions (×10^{-7} mol/g_{cat}): (a) 0, (b) 22, (c) 110, and (d) 550.

On the other hand, as shown in Fig. 3, in the case of chemical doping using the sol–gel method, the Fe ions doped TiO_2 exhibit only a small shift, in spite of much larger amounts of doping of Fe ions as compared with the ion-implantation method.

Fig. 4 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 peak and post-edge shoulder. And in the FT-EXAFS, a peak due to the neighboring titanium atoms in TiO_2 lattice (Fe–O–Ti) can be observed as well as a peak due to the neighboring oxygen atoms (Fe–O). These peak positions are different from those of α-Fe_2O_3 and α-FeOOH (Fe–O–Fe, Fe–O), respectively. Furthermore, the Fe ion-implanted TiO_2 shows a single Fe–O–Fe peak, while a intense shoulder was observed in Fe–O–Fe peak with α-Fe_2O_3 and α-FeOOH. 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. The same results that the implanted metal ions are substituted with lattice Ti^{4+} ions in the lattice of TiO_2 have been observed by the XAFS analysis with V ion- and Cr ion-implanted TiO_2 samples [17]. These results obtained using XAFS technique suggest that the substitution of octahedrally coordinated Ti^{4+} ions in

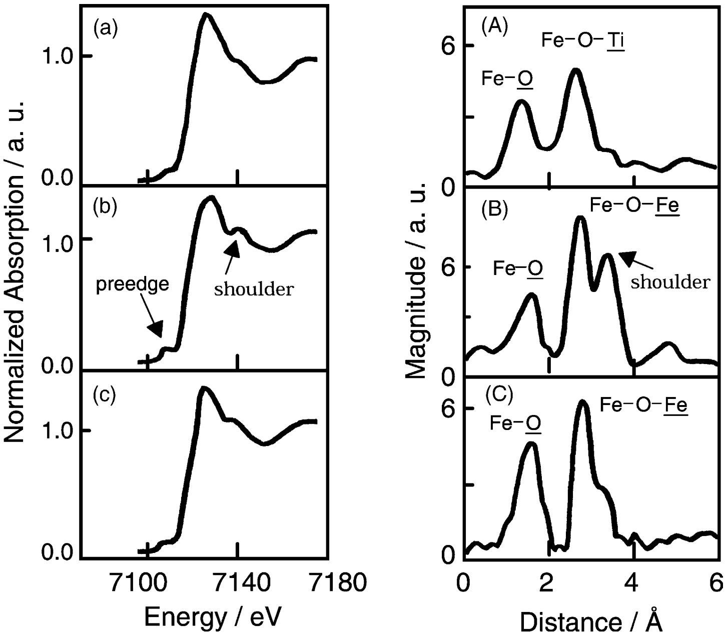

Fig. 4. The XANES (left) and Fourier transforms EXAFS (right) spectra of the Fe ion-implanted TiO_2 (a, A), α-Fe_2O_3 (b, B) and α-FeOOH (c, C). Ion acceleration energy: 150 keV. Amounts of implanted Fe ions: 13.2×10^{-7} mol/g_{cat}.

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.

As shown in Fig. 5, the visible light irradiation ($\lambda > 450$ nm) of the Fe 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 is finally decomposed into CO_2 and H_2O. The formation of these products was not detected under dark condition. On the other hand, the unimplanted original TiO_2 photocatalyst did not exhibit any photocatalytic reactivity under visible light irradiation. 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 ($\lambda > 350$ nm), the photocatalytic reactivity for the degradation of 2-propanol on the metal ion-implanted TiO_2 (amounts of Fe ions: 6.6×10^{-7} mol $g_{cat}{}^{-1}$, initial conversion of 2-propanol: 59 μmol h^{-1} $g_{cat}{}^{-1}$) was similar to that on the unimplanted original TiO_2 photocatalyst

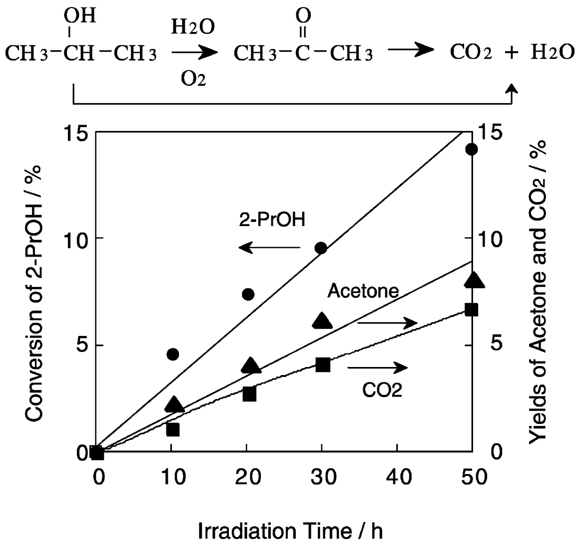

Fig. 5. The reaction time profiles of the photocatalytic oxidative degradation of 2-propanol diluted in water on the Fe ion-implanted TiO_2 photocatalysts under visible light irradiation ($\lambda > 450$ nm). Ion acceleration energy: 150 keV. Amounts of implanted Fe ions: 13.2×10^{-7} mol/g_{cat}.

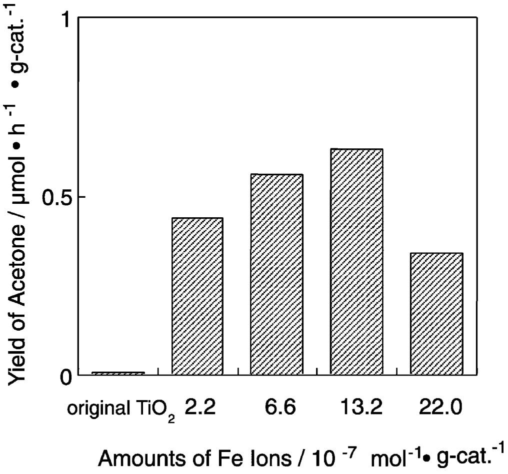

Fig. 6. The effect of the amounts of implanted Fe ions on the specific photocatalytic reactivities of the Fe ion-implanted TiO_2 photocatalysts for the oxidative degradation of 2-propanol diluted in water under visible light irradiation ($\lambda > 450$ nm). Amounts of implanted Fe ions ($\times 10^{-7}$ mol/g_{cat}): 2.2, 6.6, 13.2, and 22.0.

($56\,\mu mol\,h^{-1}\,{g_{cat}}^{-1}$), indicating that the implanted metal ions do not work as the electron–hole recombination center.

Fig. 6 shows the effect of the amounts of Fe ions implanted into TiO_2 catalysts on the photocatalytic reactivity under visible light irradiation ($\lambda > 450$ nm). Although the unimplanted original TiO_2 photocatalyst did not exhibit any photocatalytic reactivity under visible light irradiation, the Fe ions implanted TiO_2 photocatalysts exhibit a photocatalytic reactivity for the oxidative degradation of 2-propanol under visible light irradiation. It was found that the photocatalytic reactivity under visible light irradiation increased, as increasing the amounts of Fe ions implanted. However, after reaching the maximum reactivity, the reactivity of the photocatalysts under visible light irradiation decreased by further implantation of Fe ions. These results show that the reactivity of TiO_2 photocatalysts implanted with Fe ions under visible light irradiation strongly depends on the amounts of Fe ions implanted.

On the other hand, TiO_2 photocatalysts chemically doped with Fe ions by the sol–gel method exhibited very little photocatalytic reactivity under visible light irradiation and was also found that the photocatalytic reactivity under UV light irradiation (bandgap irradiation) decreased dramatically as compared with the original pure TiO_2 photocatalyst.

4. Conclusions

The Fe ion-implanted TiO_2 catalysts enable the absorption of visible light up to a wavelength of 400–600 nm and that successfully enable photocatalytic reaction in the liquid-phase systems. The photocatalytic reactivity strongly depends on the amount of Fe ions. The present research has opened the way to many innovative possibility, significantly addressed urgent environmental concerns, and can also be considered an important breakthrough in the utilization of solar energy.

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