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Characterization of metal ion-implanted titanium oxide photocatalysts operating under visible light irradiation

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The metal ion-implantation of titanium oxide with metal ions (Cr^+ or V^+) at high energy acceleration and the subsequent calcination of these metal ion-implanted TiO_2 in oxygen at around 725 K resulted in a large shift in the absorption spectra toward visible light regions. These catalysts exhibited effective and remarkable photocatalytic reactivity for various reactions such as the decomposition of NO into N_2, O_2 and N_2O at 275 K not only under UV but also under visible light irradiation. XAFS, ESR and UV-Vis studies have revealed that the implanted metal ions (Cr^+ or V^+) are located at the lattice positions of Ti^{4+} in TiO_2 and stabilized as Cr^{3+} or (V^{3+} or V^{4+}) species after the calcination of the sample in O_2 at around 775 K. Thus, these spectroscopic studies show that the presence of these substitutional metal ion species are, in fact, responsible for the large shift in the absorption spectra of these catalysts toward visible light regions.

Keywords: Photocatalyst; TiO_2; Metal ion-implantation; Visible light; NO decomposition; XAFS

1. INTRODUCTION

Recently, investigations to address urgent environmental concerns using various kinds of titanium oxide photocatalysts have been actively carried out [1-3]. However, conventional titanium oxides such as TiO_2 powdered semiconducting catalysts cannot utilize visible light and make use of only the 3-4% of the solar beams that reach the earth, necessitating the use of an ultraviolet light source such as a mercury lamp.

In this study, the development of TiO_2 photocatalysts which absorb visible light and are thus able to operate under visible light irradiation has been successfully carried out using a high energy ion-implantation method [3,4] and the local structures of the metal ion-implanted TiO_2 have been clarified using XAFS analysis.

2. EXPERIMENTAL

The TiO_2 catalyst was supplied by the Catalysis Society of Japan as a standard reference catalyst (JRC-TIO-4: surface area ≈ 50 m^2/g, band gap ≈ 3.50 eV, ~80% anatase, ~20% rutile). The implantation of the metal ions (Cr^+ or V^+) to the TiO_2 photocatalysts was carried out by using an ion-implanter consisting of a metal ion source, mass analyzer, high voltage ion accelerator (150 keV), and a high vacuum pump. The Cr-impregnated TiO_2 was prepared by impregnating TiO_2 with an aqueous solution of $Cr(NO_3)\cdot 9H_2O$. UV irradiation of the catalysts in the presence of NO (12.8 μmol) was carried out using a 75-W high-pressure Hg lamp ($\lambda > 450$ nm and $\lambda \sim 380$ nm) at 275 K. The reaction products were analyzed by gas chromatography. The UV-VIS spectra (diffuse reflectance) of the catalysts were measured using a Shimazu UV-2200A spectrophotometer at 295 K. ESR spectra were recorded at 77 K with a Bruker ESP300E spectrometer (X-band). The XAFS spectra were obtained at the BL-7C facility of the Photon Factory at the National Laboratory for High Energy Physics (KEK-PF) in Tsukuba with a ring energy of 2.5 GeV. The Cr K-edge absorption spectra were recorded in the fluorescence mode at 295 K with an Si(111) two-crystal monochromator. The normalized spectra were obtained by a procedure described in previous literature [5], and Fourier transformations were performed on k^3-weighted EXAFS oscillations in the range of 3-12 $Å^{-1}$.

3. RESULTS AND DISCUSSION

As shown in Fig.1, the absorption band of the TiO_2 doped with Cr ions by the ion-implantation has been found to shift to visible light regions, the extent depending on the amount of Cr ions implanted. The Cr ions implanted within the bulk of TiO_2 can modify the electronic properties of the TiO_2 surface. It can be expected that photocatalytic reactions could be observed under visible light on these Cr ion-implanted TiO_2 catalysts.

Under UV light irradiation, the photocatalytic activity in NO decomposition on Cr ion-implanted TiO_2 is similar to the TiO_2 photocatalyst, indicating that the implanted Cr ions do not work as the electron-hole recombination center in the Cr ion-implanted photocatalysts.

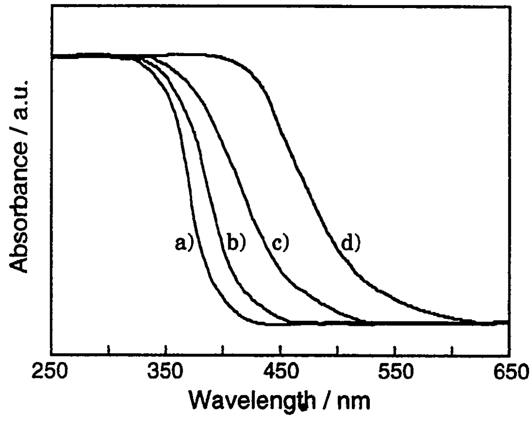

Fig. 1 UV-VIS spectra (diffuse reflectance) of the TiO_2 (a) and the TiO_2 implanted with Cr ions (b-d). (amounts of Cr ion implanted: (in mol/g-TiO_2) b: 2.2 x 10^{-7}, c: 6.6 x 10^{-7}, d: 1.3 x 10^{-6}).

Figure 2 shows the time profiles of the photocatalytic decomposition of NO into N_2, O_2 and N_2O on the TiO_2 and Cr ion-implanted TiO_2 catalysts under visible light irradiation ($\lambda > 450$ nm). Visible light irradiation of the Cr ion-implanted TiO_2 in the presence of NO at 275 K leads to the direct decomposition of NO into N_2, O_2 and N_2O with a good linearity to the irradiation time. Under the same conditions of visible light irradiation, these photocatalytic reactions do not proceed on the un-implanted pure TiO_2 photocatalyst. Thus, it can be seen that the implantation of ions was the determining factor in the use of visible light.

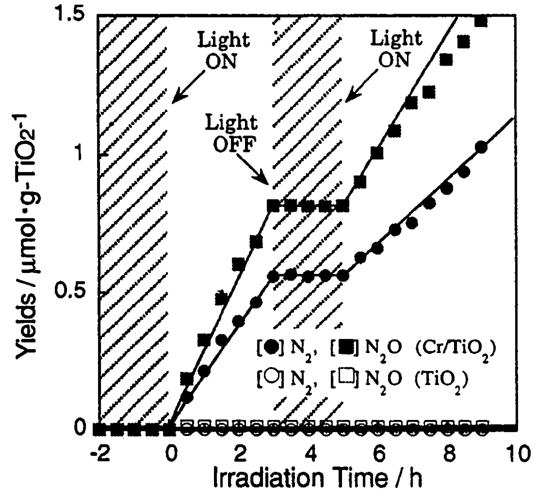

Fig. 2 Reaction time profiles of the photocatalytic decomposition of NO into N_2, O_2 and N_2O on the Cr ion-implanted TiO_2 under visible light irradiation (λ > 450 nm).

Figure 3 shows the XANES and Fourier transforms of EXAFS (FT-EXAFS) spectra of the Cr ion-implanted TiO_2 and Cr-impregnated TiO_2. The Cr ion-implanted TiO_2 exhibits a XANES spectrum similar to Cr_2O_3 without any intense preedge peaks. And in the FT-EXAFS, only a single peak due to the neighboring oxygen atoms (Cr-O) can be observed. These results indicate that Cr ions are highly dispersed in the lattice of TiO_2 having octahedral coordination. Cr ions exist species substituted with lattice Ti^{4+} ions. On the other hand, the Cr impregnated TiO_2 exhibits a preedge peak which is characteristic of a Cr-oxide species in tetrahedral coordination and the intensity of the peak due to the neighboring Cr atoms (Cr-O-Cr) in the FT-EXAFS spectrum becomes strong, indicating that the catalyst consists of a mixture of tetrahedrally and octahedrally coordinated Cr-oxide species (Cr_2O_3-like cluster).

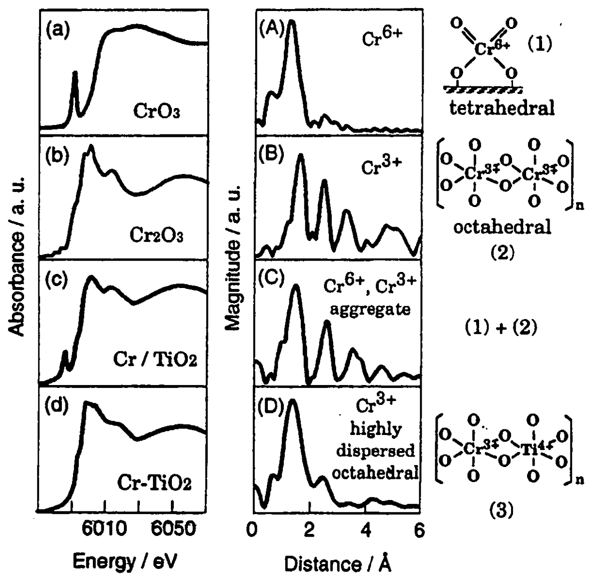

Fig. 3 The Cr K-edge XANES (a-d) and FT-EXAFS (A-D) spectra of CrO_3 (a, A), Cr_2O_3 (b, B), Cr ion impregnated TiO_2 (c, C) and Cr ion-implanted TiO_2 (d, D).as isolated Cr^{3+}

V ion-implanted TiO_2 can also adsorb visible light and shows efficient photocatalytic reactivity under visible light irradiation. V ion-implanted TiO_2 shows a weak preedge peak in its XANES spectrum (Fig.4). Considering the observation of this weak preedge peak and its peak position, it was found that V ions exist as V^{3+} or V^{4+} ions in octahedral coordination in the lattice positions of TiO_2. The observation of the characteristic ESR spectra which is assigned to the presence of V^{4+} ions substituted to the lattice Ti^{4+} ions also supported these findings [4].

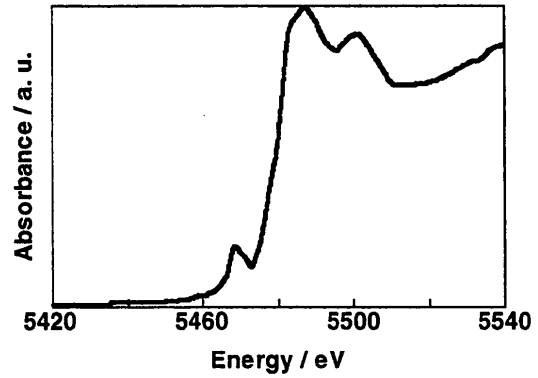

Fig. 4 The V K-edge XANES spectrum of V ion-implanted TiO_2.

4. CONCLUSIONS

The present studies clearly show that, after calcination in oxygen at around 723 K, TiO_2 catalysts incorporated with transition metal ions by a high energy metal ion-implantation method, specifically Cr or V ion-implanted TiO_2, allow the efficient absorption of visible light, thus enabling the photocatalysts to operate effectively under visible light or solar light irradiation. The implanted metal ions (Cr^+ or V^+) were located at the lattice position of TiO_2 and stabilized as Cr^{3+} or (V^{3+} or V^{4+}) species after the calcination of the sample in O_2 at around 775 K. The presence of these substitutional metal ion species were found to be responsible for the large shift in the absorption spectra of the metal ion-implanted titanium oxide catalysts toward visible light regions.

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