Catalysis Letters Vol. 98, No. 4, December 2004 (© 2004)

Photocatalytic activity of a TiO_2 photocatalyst doped with C^{4+} and S^{4+} ions having a rutile phase under visible light

Teruhisa Ohno*, Toshiki Tsubota, Maki Toyofuku and Ryoji Inaba

Department of Material Science, Faculty of Engineering, Kyushu Institute of Technology, 1-1 Sensu-icho, Tobata, Kitakyushu 804-8550, Japan

Received 7 June 2004; acccepted 11 September 2004

C^{4+} and S^{4+}-codoped titanium dioxide (TiO_2) having a rutile phase was prepared. By doping C^{4+} and S^{4+} ions into a TiO_2 lattice, the absorption edge of rutile TiO_2 powder was largely shifted from 400 to 700 nm. 2-Methylpyridine and methyleneblue were photocatalytically oxidized at high efficiency on C^{4+} and S^{4+}-doped TiO_2 under visible light at a wavelength longer than 5 nm.

KEY WORDS: TiO_2 photocatalyst; photocatalysis with visible light.

1. Introduction

Titanium dioxide (TiO_2)-mediated heterogeneous photocatalysis has attracted much attention because of its potential applications to decomposition of pollutants in water and air [1,2]. In these applications, anatase TiO_2 powders consisting of particles with large surface areas are used as photocatalysts. These powders are advantageous for absorption of compounds included in the reaction system at low concentrations. In contrast to the case of anatase TiO_2 photocatalysts, oxidation of water, which is difficult to oxidize, proceeds efficiently on large rutile TiO_2 particles [3]. Anatase TiO_2 photocatalysts do not have photocatalytic activity for oxidation of water.

Although titanium dioxide, the most promising photocatalyst, is now used in various practical applications [1,2], only a small UV fraction of solar light, about 2–3%, can be utilized because of its large band gap of 3.2 eV. Therefore, the development of a TiO_2 photocatalyst that shows a high level of activity under visible light is needed. N, S, or C anion-doped TiO_2 photocatalysts having an anatase form that shows a relatively high level of activity under visible light irradiation have been reported [4–8]. Sakthivel *et al.* succeeded in preparing TiO2 photocatalysts containing some carbon species that show photocatalytic activity under visible light [9]. We have also reported the preparation of S cation-doped TiO_2 having an anatase phase and its photocatalytic activity [10,11]. The absorbance of S cation-doped TiO_2 in the visible region is larger than that of N-, C- or S anion-doped TiO_2 and the photocatalytic activity level of S cation-doped TiO_2 is relatively high under visible light compared to that of N-, C- or S anion-doped TiO_2. It should be noted that S atoms were incorporated into the lattice of TiO_2 as cations and were thought to be replaced by Ti ions in the case of S-cation doped TiO_2.

We have succeeded in preparing a TiO_2 photocatalyst doped with C^{4+} and S^{4+} having a rutile phase in order to increase absorbance in the visible region, resulting in improvement in photocatalytic activity under visible light irradiation. There has been no report on fabrication of pure C^{4+} and S^{4+}-codoped TiO_2 having a rutile phase and its photocatalytic activity under visible light irradiation.

In this paper, we describe the procedure for preparation of and the photocatalytic activities of C^{4+} and S^{4+}-codoped TiO_2 having a rutile phase for oxidation of 2-methylpyridine and methylene blue under visible light irradiation.

2. Experimental

2.1. Materials and instruments

TiO_2 powder having a rutile crystal structure was obtained from Ishihara Sangyo (ST-01) and TAYCA (MT-150A). The content of anatase and relative surface area of ST-01 particles were 100% and 320 m^2/g, respectively, and those of MT-150A particles were 0% and 88.0 m^2/g, respectively. Thiourea was obtained from Tokyo Chemical Industry Co. Ltd. Methylene blue, 2-propanol, and acetone were purchased from Wako Pure Chemical Industry. Other chemicals were obtained from commercial sources as guaranteed reagents and were used without further purification. The crystal structures of TiO_2 powders were determined from XRD patterns measured by using an X-ray diffractometer (Philips, X'Pert-MRD) with a Cu target K α-ray ($\lambda = 1.5405$ Å). The relative surface areas of the powders were determined by using a surface area analyzer (Micromeritics, FlowSorb II 2300). The

---

*To whom correspondence should be addressed.

1011-372X/04/1200–0255/0 © 2004 Plenum Publishing Corporation

absorption and diffuse reflection spectra were measured using a Shimadzu UV-2500PC spectrophotometer. X-ray photoelectron spectra (XPS) of the TiO_2 powders were measured using a Shimadzu ESCAIOOO photoelectron spectrometer with an Al K source (1486.6 eV). The shift of binding energy due to relative surface charging was corrected using the C 1s level at 285 eV as an internal standard. The XPS peaks were assumed to have Gaussian line shapes and were resolved into components by a non-linear least squares procedure after proper subtraction of the baseline.

2.2. Preparation of C^{4+} and S^{4+}-codoped TiO_2 powder

TiO_2 powders doped with C^{4+} and S^{4+} having a rutile phase were prepared as follows. Thiourea (15.2 g) was mixed with 4.0 g of rutile TiO_2 powder (MT-150A) in an agate mortar. The mixed powder was packed in a lidded double alumina crucible and calcined at 400 and 500 °C under aerated conditions for 5 h. After calcination, the powder was washed with distilled water. The resulting samples were dark yellow in color and were found to have a homogenous rutile phase. For TiO_2 powder calcined at a temperature higher than 600 °C, no absorbance in the visible region was observed. The surface areas of the resulting powders calcined at 400 and 500 °C were 70.7, and 56.3 m^2/g, respectively. The relative surface area decreased with increase in the calcination temperature.

2.3. Photocatalytic decomposition of methylene blue upon photo irradiation of TiO_2 powder

Photocatalytic activity of TiO_2 powder was estimated by measuring the decomposition rate of methylene blue (50 mmol dm^{-3}) in an aqueous solution (5 ml) containing 100 mg of the TiO_2 photocatalyst. S-doped TiO_2 or pure TiO_2 powder (ST-01) was used as the photocatalyst. The TiO_2 suspension was sonicated before the reaction and rotated using a magnetic stirrer. The suspension was photoirradiated using a 1000 W Xe lamp (EIKI Industrial Co. Ltd., EX-1000GT), which emits both UV and Visible light over a wide wavelength with an integrated photon flux of 3.1×10^{-5} einsteins s^{-1} cm^{-2} between 350 and 540 nm. To limit the irradiation wavelength, the light beam was passed through a UV-34, L-42, Y-44, Y-50 or Y-54 filter (Kenko Co.) to cut-off wavelengths shorter than 340, 420, 440 or 500 nm, respectively. Fine stainless meshes were used as neutral density filters to adjust the irradiation intensity. The amounts of methylene blue that remained after photoirradiation were determined using a UV-Vis spectrophotometer.

2.4. Photocatalytic oxidation of 2-methylpyridine upon photo irradiation of TiO_2 powder

Components of the experimental system, such as light source and filters, used for oxidation of 2-methylpyridine were the same as those used for photocatalytic degradation of methylene blue. Photocatalytic oxidation of 2-methylpyridine (1.0 mol dm^{-3}) in an aqueous solution (5 ml) containing 100 mg of the TiO_2 photocatalyst proceeded under photoirradiation at wavelengths of a wide range. After photoirradiation for certain time periods, solutions were analyzed with high-performance liquid chromatographs (HPLC, Shimadzu LC-6A System) equipped with an TSK-GEL ODS-80Ts column. A mixture of aqueous solution (K_2HPO_4:2.5 mmol dm^{-3} ; KH_2PO_4:2.5 mmol dm^{-3} ; $NaClO_4$:0.1 mmol dm^{-3}) and methanol (9:1) was used as an eluent.

3. Results and discussion

3.1. Physical properties of C^{4+} and S^{4+}-codoped TiO_2 powder

In order to investigate the chemical states of C, N and S atoms incorporated into TiO_2, C 1s, N ls and S 2p binding energies were measured by X-ray photoemission spectroscopy (XPS). The results are shown in figure 1. From XPS analyses, no peak assigned to N was found. Consequently, the resulting powders contained C and S atoms instead of N atoms. Peaks at 288 eV were observed by XPS measurements of the C 1s binding energy of the resulting powders calcined at 400 and 500 °C. This peak suggests the presence of carbonate species [12]. A peak around 168 eV, which is assigned to

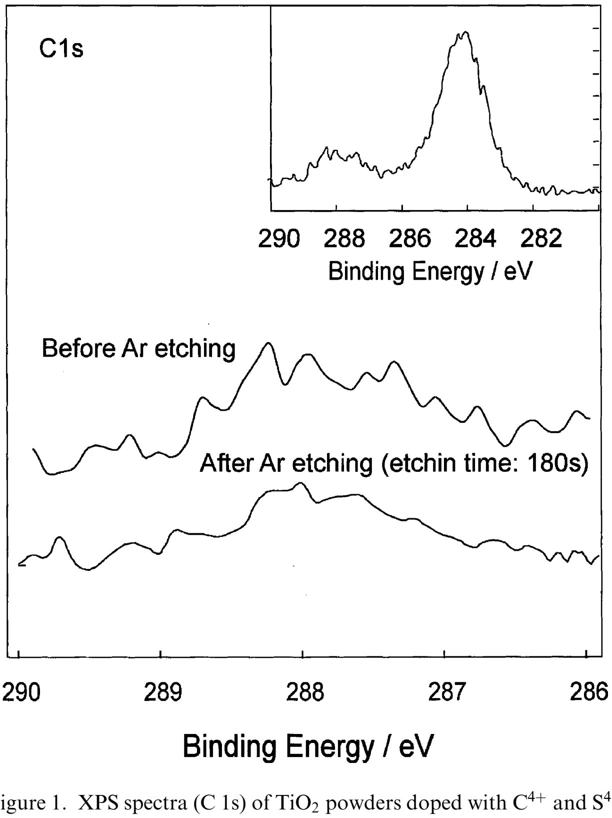

Figure 1. XPS spectra (C 1s) of TiO_2 powders doped with C^{4+} and S^{4+} having a rutile phase at 400 °C.

S^{4+} states [13], also appears after calcination under aerated conditions as shown in figure 1. These peaks remained after Ar^+ ion etching of the sample. These results strongly indicate that C^{4+} and S^{4+} ions are incorporated into the bulk phase of TiO_2. The atomic content of S^{4+} in the TiO_2 powder calcined at 400 °C is about 0.1%. The amount of C^{4+} in the TiO_2 particles is about 0.2%. These assignments are supported by the IR spectrum of C^{4+} and S^{4+}-codoped TiO_2 powder exhibiting low-intensity peaks at 1738, 1096, and 798 cm^{-1} that are indicative for the carbonate ion [14]. On the other hand, we did not observe IR peaks assigned to SO_2 because the amount of S^{4+} atoms is very small and its IR peaks are considered to be very weak. The crystal structure of TiO_2 powders were found to be only a rutile phase using XRD measurements. No peaks assigned to Ti–C or Ti–S were found by XRD measurements.

The diffuse reflectance spectra of C^{4+} and S^{4+}-codoped TiO_2 powder calcined at 400 and 500 °C together with those of pure rutile TiO_2 powder (MT-150A) and pure anatase TiO_2 powder (ST-01) are shown in figure 2. Photoabsorption in the visible region of C^{4+} and S^{4+}-codoped TiO_2 powders was greatly increased compared to that of original TiO_2 powder (MT-150A). With increase in the calcination temperature above 500 °C, absorption in the visible region rapidly disappeared.

Photocatalytic activity of the C^{4+} and S^{4+}-codoped TiO_2 powder was evaluated by measuring the rates of oxidation of 2-methylpyridine and decomposition of methylene blue. Methylene blue (50 mmol dm^{-3}) was dissolved in an aqueous solution (5 ml) containing 100 mg of the TiO_2 photocatalyst. C^{4+} and S^{4+}-codoped TiO_2 powder or a fine TiO_2 powder (ST-01) was used as the photocatalyst. A 500-W Xe lamp was used as the light source, and the short-wavelength components of the light were removed using cutoff glass filters with different cutoff wavelengths. Under photoirradiation at wavelengths longer than 350 nm, the photocatalytic activity level of C^{4+} and S^{4+}-codoped TiO_2 was about two-times higher than that of pure TiO_2 powder (ST-01). Furthermore, under visible light irradiation at wavelengths longer than 440 nm, only C^{4+} and S^{4+} -codoped TiO_2 powder showed a high level of activity. Figure 3 shows the activities of C^{4+} and S^{4+}-codoped TiO_2(calcined at 400 and 500 °C for 5 h) and pure anatase TiO_2 (ST-Ol) as a function of the cutoff wavelengths of the glass filters. No degradation of methylene blue was observed in the absence of TiO_2 powder or without irradiation.

In the case of oxidation of 2-methylpyridine, 2-pyridine carboxy aldehyde and 2-pyridine carboxylic acid were obtained as main products. It should be noted that C^{4+} and S^{4+}-codoped TiO_2 showed about 10–12-times greater activity than that of ST-01, which usually shows a higher activity level than most commercially available TiO_2 photocatalysts for oxidation a pollutant in air or water, even under photoirradiation at a wavelength longer than 350 nm as shown in figure 4. Furthermore, under visible light irradiation at wavelengths longer than 440 nm, only C^{4+} and S^{4+}-codoped TiO_2 powder showed a high level of activity. No

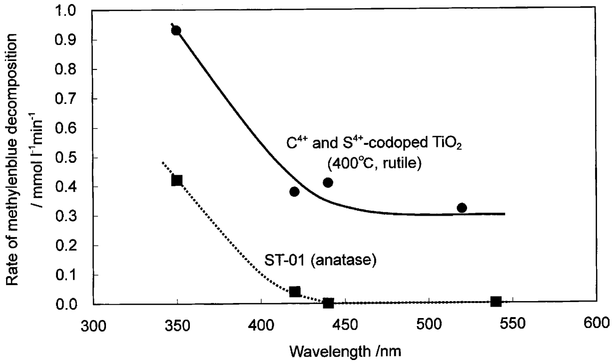

Figure 3. Decomposition of methylene blue using C^{4+} and S^{4+}-codoped TiO_2 powder having a rutile phase calcined at 400 and 500 °C and pure TiO_2 (ST-01, anatase).

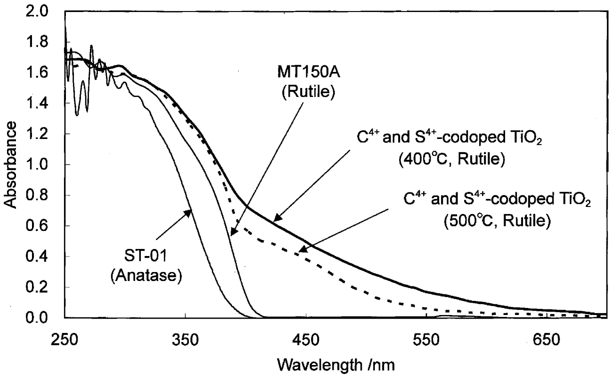

Figure 2. Optical absorbance spectra of C^{4+} and S^{4+}-codoped TiO_2 powder having a rutile phase calcined at 400 and 500 °C and pure TiO_2 (ST-01, anatase; MT-I50A, rutile).

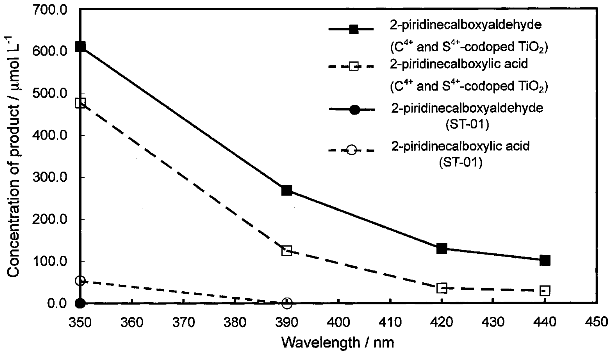

Figure 4. Oxidation of 2-methylpyridine using C^{4+} and S^{4+}-codoped TiO_2 powder having a rutile phase calcined at 400 and 500 °C and pure TiO_2 (ST-01, anatase).

oxidation of 2-methylpyridine was observed in the absence of TiO_2 powder or without irradiation.

4. Summary

We succeeded in preparing C^{4+} and S^{4+}-codoped TiO_2 photocatalysts having a rutile phase. Oxidation states of S and C atoms incorporated into the lattice of TiO_2 are both mainly tetravalent. The activity of C^{4+} and S^{4+}-codoped TiO_2 having a rutile phase for oxidation of methylene blue and 2-methylpyridine is much stronger than that of a fine anatase TiO_2 photocatalyst (ST-01) under a wide range of incident light including the visible region. We expect that the activity will be greatly improved by optimizing conditions for preparation of the C^{4+} and S^{4+}-codoped TiO_2 powders having a rutile phase.

Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (417) from the Ministry of Education, Culture, Science, and Technology (MEXT), Japan.

References

[1] M.R. Hoffman, S.T. Martin, W. Choi and D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
[2] F. Soana, M. Strini, L. Cermenati and A. Albini, J. Chem. Soc. Perkin Trans. 2 (2000) 699.
[3] T. Ohno, D. Haga, K. Fujihara, K. Kaizaki and M. Matumura, J. Phys. Chem. B 101 (1997) 6415 errata, 101 (1997) 1065.
[4] R. Asahi, T. Morikawa, T. Ohwaki, A. Aoki and Y. Taga, Science 293 (2001) 269.
[5] Y. Sakatani, K. Okusato, H. Koike and H. Ando, Photocatalysis 4 (2001) 51.
[6] T. Ihara, M. Ando and S. Sugihara, Photocatalysis 5 (2001) 19.
[7] T. Umebayashi, T. Yamaki, H. Ito and K. Asai, Appl. Phys. Lett. 81 (2002) 454.
[8] H. Irie, Y. Watanabe and K. Hashimoto, Chem. Lett. 32 (2003) 772.
[9] S. Sakthivel and H. Kisch, Angew. Chem. Int. Ed., 42 (2003) 4908.
[10] T. Ohno, T. Mitsui and M. Matsumura, Chem. Lett. 32 (2003) 364.
[11] T. Ohno, M. Akiyoshi, T. Umebayashi, K. Asai, T. Mitsui and M. Matsumura, Appl. Catal. A., General, 265 (2004) 115.
[12] E. Papirer, R. Lacroix, J.-B. Donnet, G. Nanse and P. Fioux, Carbon 33 (1995) 63.
[13] D.I. Sayago, P. Serrano, O. Bonme, A. Goldoni, G. Paolucci, E. Roman and J.A. Martin-Gago, Phys. Rev. B 64 (2001) 205402.
[14] S. Gablenz, H.-P. Abicht, E. Pippel, O. Lichtenberger and J. Woltersdorf, J. Eur. Ceram. Soc. 20 (2000) 1053.