Catalysis Letters, Vol. 113, Nos. 3–4, February 2007 (© 2007)
DOI: 10.1007/s10562-007-9029-5

Effect of the addition of a small amount of vanadium on the photocatalytic activities of N- and Si- co-doped titanias under visible-light irradiation

Hirotaka Ozaki, Shinji Iwamoto,* and Masashi Inoue

Department of Energy and Hydrocarbon Chemistry Graduate School of Engineering, Kyoto University, Katsura, Kyoto 615-8510, Japan

Received 1 November 2006; accepted 15 December 2006

Si-doped titanias with a Si/Ti charged ratio of 0.2 was prepared by thermal reactions of titanium tetraisopropoxide and tetraethyl orthosilicate in 1,4-butanediol at 300 °C (glycothermal reaction) and N- and Si- co-doped titanias were prepared by heating the thus-obtained Si-doped titanias in an NH_3 flow. N- and Si- co-doped titanias had a stronger absorption in a visible light region of 400–550 nm, and exhibited high photocatalytic activities for decomposition of acetaldehyde under visible-light irradiation. In this study, N- and Si- co-doped titanias were further modified with vanadium by an impregnation method using an ammonium vanadate solution, and the obtained catalysts were characterized by XRD, BET surface area measurement, UV-vis, and ESR. Photocatalytic decomposition of acetaldehyde using the V-loaded N- and Si- co-doped titanias was examined and it was demonstrated that a very small amount of V-loading (V/Ti = 0.0001–0.001) significantly enhanced the photocatalytic activity under visible-light irradiation.

KEY WORDS: Si-doped titania; nitrogen-doping; visible-light photocatalyst; glycothermal method; V-loading.

1. Introduction

Numerous studies have been reported in the last decade on the photodecomposition of organic pollutants using semiconductor materials as photocatalysts. Titanium dioxide (TiO_2) is one of the most widely studied materials [1, 2] because of its favorable physical, chemical and optoelectronic properties. The utilization of TiO_2 photocatalysts is, however, limited only under ultraviolet (UV) irradiation because of the relatively wide band gap energies, for instance, 3.0 eV for rutile and 3.2 eV for anatase.

A number of researches on the development of visible-light sensitive photocatalysts has been made in order to utilize the solar energy efficiently. A nitrogen-doped TiO_2 material with a visible light responsibility was reported by Sato for the first time in 1986 [3], and recently, several groups reported the visible-light responsibility of N-doped TiO_2 materials prepared by different methods [4–9]. We recently reported that when nanocrystalline Si-doped titanias prepared by thermal reactions of titanium tetraisopropoxide and tetraethyl orthosilicate in 1,4-butanediol (glycothermal reaction) were heated in NH_3 at high temperatures, N- and Si- co-doped titanias with higher nitrogen contents were obtained, and that the obtained samples exhibited high photocatalytic activities for decomposition of acetaldehyde under visible-light irradiation [10]. Several transition-metal-ion dopants in TiO_2 have been investigated previously with regard to the photocatalytic activity under UV light irradiation [11–13]. However, studies on the effect of transition metal modification for N-doped TiO_2, which exhibits visible-light sensitivity, are relatively few [14]. In this study, we examined the visible-light induced photocatalytic activity of the N- and Si- co-doped titanias modified with a small amount of vanadium.

2. Experimental

Si-doped titania with a Si/Ti charged ratio of 0.2 was prepared by the glycothermal method and collected as a xerogel form as described in our previous report [15]. The as-synthesized product was calcined in a box furnace in air at 500 °C for 30 min to remove the surface organic moieties. The thus-obtained sample was designated as Si(0.2)–TiO_2. Si(0.2)–TiO_2 was heated in a 100 mL/min flow of argon up to 600 °C at a rate of about 10 °C/min and then exposed to NH_3 (100 mL/min) for 1 h, followed by annealing at 500 °C in air for 30 min (designated as N–Si(0.2)–TiO_2). Vanadium loading onto Si(0.2)–TiO_2 and N–Si(0.2)–TiO_2 was carried out by an impregnation method: Si(0.2)–TiO_2 or N–Si(0.2)–TiO_2 was added to an aqueous solution of ammonium vanadate (NH_4VO_3). Then, the samples were dried and calcined at 500 °C for 30 min. The

---

*To whom correspondence should be addressed.
E-mail: iwamoto@scl.kyoto-u.ac.jp

1011-372X/07/0200–0095/0

thus-obtained V-modified catalysts are designated as V(x)–Si(0.2)–TiO_2 or V(x)–N–Si(0.2)–TiO_2, where x is V/Ti charged atomic ratio, $0 \leq x \leq 0.10$.

The UV–vis absorption spectra were recorded on a Shimadzu MPS-2000 spectrophotometer. Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XD-D1 diffractometer using CuKα radiation and a carbon-monochromator. The specific surface areas of the samples were determined by the BET single-point method on the basis of the nitrogen uptake measured at 77 K. X-band ESR spectra were recorded at 123 K under an aerated condition with a JEOL JES-SRE2X spectrometer equipped with a 500 W mercury lamp.

Photocatalytic activity was evaluated by decomposition of acetaldehyde. The reaction was carried out in a closed glass vessel (1.0 L). The catalyst (0.2 g) dispersed on a 90 mm φ glass filter was placed in the vessel and 0.2 mmol acetaldehyde was injected in it. The vessel was placed in the dark for 1 h and then visible light was irradiated using a 300 W xenon lamp (Optical Modulex SX-UI300XQ, Ushio Inc.) through a UV cut-off filter (L-42, Asahi Technoglass Co. Ltd.) and an infrared cut-off filter (Super Cold Filter, Ushio Inc.). After a certain period of irradiation, the CO_2 concentration was measured by a gas chromatograph, Shimadzu GC-8A. The amount of CO_2 formed was calculated by subtracting the initial amount of CO_2 in the vessel.

3. Results and discussion

The XRD patterns of Si(0.2)–TiO_2 and N–Si(0.2)–TiO_2 showed diffraction peaks due to the anatase structure. Crystallite sizes of these two samples were identical (10 nm) and their BET surface areas were 164 and 158 m^2/g, respectively, indicating the obtained products were well-dispersed nanocrystals. After the V loading, XRD patterns as well as BET surface areas did not change significantly; for example, crystallite size and BET surface area of V(0.001)–N–Si(.2)–TiO_2 were 10 nm and 161 m^2/g, respectively.

Si(0.2)–TiO_2 is a white powder and the color turned into vivid yellow after the NH_3 treatment and annealing. In the case of low vanadium loading with x in V(x)–N–Si(0.2)–TiO_2 less than 0.01, the color of the sample did not change significantly after the loading of vanadium. With the increase in the amount of V-loading ($x > 0.01$), the color became orange or brownish. The UV-vis absorption spectra of V(x)–Si(0.2)–TiO_2 and V(x)–N–Si(0.2)–TiO_2 are shown in figure 1a, b, respectively. Si(0.2)-TiO_2 exhibited absorption only in the UV region. With the vanadium modification, however, an expansion of the absorption into the visible region was recognized. It was reported that V_2O_5 which includes square-pyramidal VO_5 polymers or highly distorted octahedral VO_6 polymers shows an absorption at lower than 570 nm and that V^{4+} has an absorption band centered at 770 nm due to the d–d transition [16, 17]. Therefore, the spectra suggest the presence both of V^{5+} and V^{4+} in the samples. As for N–Si(0.2)–TiO_2 (i.e., $x = 0$), the catalyst had a stronger absorption band at 400–550 nm, which is attributed to the doped nitrogen into the anatase structure. The UV-vis spectra of V(x)–N–Si(0.2)–TiO_2 with x lower than 0.01 were almost same as that of the mother material, N–Si(0.2)–TiO_2. For V(x)–N–Si(0.2)–TiO_2 with higher x, an broad absorption at visible light region (> 400 nm) was also observed.

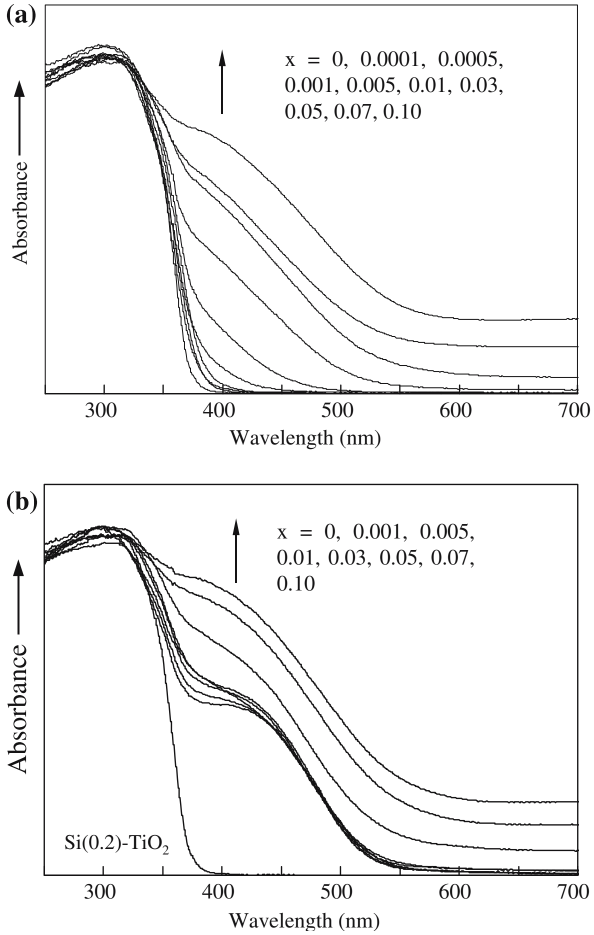

Fig. 1 UV-vis spectra of: (a) V(x)–Si(0.2)–TiO_2 and (b) V(x)–N–Si(0.2)–TiO_2.

Figure 2 shows the CO_2 generation due to the photocatalytic oxidation of acetaldehyde under visible light irradiation using V(0.01)–N–Si(0.2)–TiO_2 and N–Si(0.2)–TiO_2. In the previous study, we found that N–Si(0.1)–TiO_2 exhibited about two times higher photocatalytic activity than that of nitrified-TiO_2 without Si modification [10], and that the photocatalytic activity was further improved, by about three times, using N–Si(0.2)–TiO_2. Compared with N–Si(0.2)–TiO_2, the V-loaded catalyst showed an apparently higher photocatalytic activity.

The photocatalytic activities of V(x)–N–Si(0.2)–TiO_2 and V(x)–Si(0.2)–TiO_2 with varied amounts of V-loading

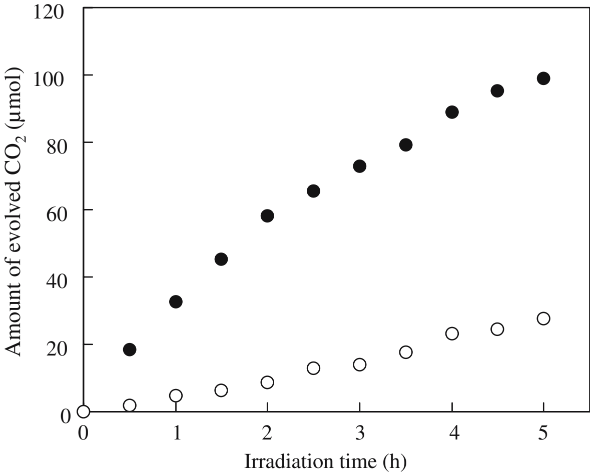

Fig. 2 Photocatalytic decomposition of acetaldehyde under visible-light irradiation on: (●), V(0.01)–N–Si(0.2)–TiO_2 and (○), N–Si(0.2)–TiO_2.

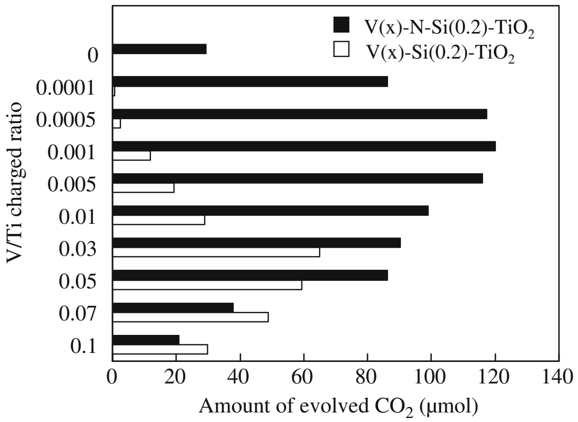

Fig. 3 Amounts of the CO_2 generated with V(x)–N–Si(0.2)–TiO_2 and V(x)–Si(0.2)–TiO_2 after 5 h of visible-light irradiation.

are shown in figure 3. For Si(0.2)–TiO_2 without N-doping, the addition of V resulted in an appearance of a certain degree of photocatalytic activity as shown in figure 3 (white bars). When the amount of V-loading was small, for example, V(0.0001)–Si(0.2)–TiO_2 and V(0.0005)–Si(0.2)–TiO_2, the catalysts had little absorption in the visible light region as shown in figure 1a, and exhibited quite low photocatalytic activities. The photocatalytic activity increased, however, gradually with the increase in the amount of V loading and reached a maximum at the V/Ti ratio of 0.03. Anpo et al. reported that the V-modified TiO_2 obtained by an ion-implantation method exhibited the visible light absorption and a photocatalytic activity for the degradation of propanol diluted in water under visible-light irradiation [18]. Appearance of visible-light responsibility of V-doped TiO_2 prepared by an impregnation method [19] and by sol-gel methods [20, 21] was also reported. Therefore, the observed visible-light sensitivity of V(x)–Si(0.2)–TiO_2 is due to the vanadium species loaded on the catalyst. On the contrary, a very small amount of V loading (V/Ti ratio = 0.0001–0.005) significantly improved the photocatalytic activity for V(x)–N–Si(0.2)–TiO_2 as shown in figure 3 with black bars, suggesting that presence of highly dispersed vanadium species has a critical role in enhancement of the photocatalytic activity. The highest photocatalytic activity was obtained with V(0.001)–N–Si(0.2)–TiO_2 which was 4 times higher than that of N–Si(0.2)–TiO_2. Since these catalysts contained quite small amounts of V, they showed similar UV-vis spectra as that of the material without the V-loading. When V/Ti ratio was increased to 0.005, the photocatalytic activity decreased slightly and further increase in the amount of V loading drastically lowered the photocatalytic activity. These results are completely different from those for V(x)–Si(0.2)–TiO_2 and suggested that the enhanced photocatalytic activity is not due to the increase in the absorption of the light in the visible region. Choi et al. examined the role of various metal ion dopants in quantum-sized TiO_2 and reported that the quantum yeild for TiO_2 was significantly improved by the V modification. Considering the energy diagram of TiO_2 and the transition metal oxides, they insisted on an ability of V-dopant as effective electron/hole traps [11]. Therefore, it is likely that the small amount of V species loaded on N- and Si- co-doped titanias fuctioned as effective electron/hole traps and inhibited the electron-hole recombination.

In order to observe an electron transfer behavior on irradiation, ESR measurement was performed (figure 4). For the non-doped sample, Si(0.2)–TiO_2, a ESR signal at $g = 2.003$ was observed under a dark condition. This signal is assigned to free electrons in TiO_2. Under UV light illumination, signals at $g = 1.990$ and 1.959 were recognized, which were assigned to trapped electrons on Ti (Ti^{3+}) [22, 23]. When the ESR measurement under UV light illumination was carried out on V(0.0001)–Si(0.2)–TiO_2, the intensity of Ti^{3+} signals decreased apparently. Increase in the amount of loaded V up to V/Ti = 0.001 resulted in the drastic decrease in the intensity of the Ti^{3+} signals, while there appeared other signals due to V^{4+}. These results suggested that photoexcited electrons in TiO_2 conduction band are transferred to V trap sites [24]. Although these ESR signals were not observed clearly in the case of the N-doped samples because of the overlapping of strong ESR signals due to paramagnetic nitrogen species in the same region, it is likely that similar electron transfer takes place and causes effective separation of the photogenerated electron–hole, consequently resulting in the improvement in the photocatalytic activity.

In summary, photocatalytic activity for decomposition of acetaldehyde under visible-light irradiation was examined using N–Si(0.2)–TiO_2 modified with V by an impregnation method. It was demonstrated that the photocatalytic activity was enhanced drastically by the

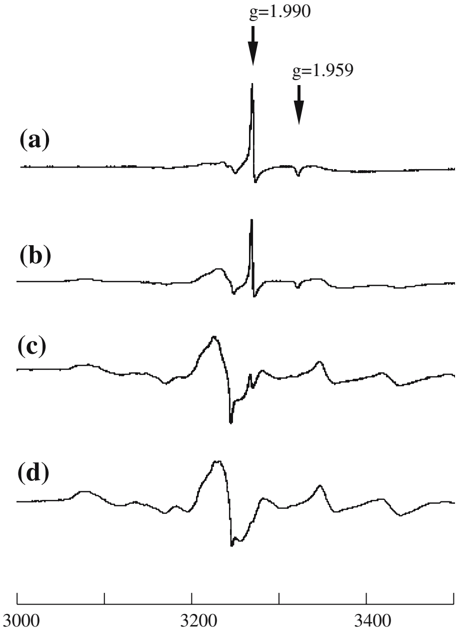

Fig. 4 ESR spectra of: (a) Si(0.2)–TiO_2, (b) V(0.0001)–Si(0.2)–TiO_2, (c) V(0.0005)–Si(0.2)–TiO_2 and (d) V(0.001)–Si(0.2)–TiO_2; under UV light illumination at 123 K.

addition of a very small amount of vanadium, V/Ti = 0.0001–0.01. V(0.001)–N–Si(0.2)–TiO_2 showed the highest photocatalytic activity, which was 4 times higher than that of N–Si(0.2)–TiO_2. Higher V-loadings, however, resulted in a decrease in the photocatalytic activity. The results suggest that highly dispersed vanadium species located on the surface of the N- and Si- co-doped titanias play a critical role as the electron trap sites. These trap sites contribute an effective separation of photoinduced electrons and holes and consequently bring about the improvement in photocatalytic activity under visible-light irradiation.

Acknowledgments

This study was supported by a Grant-in-Aid for Scientific Research (No. 16510085) from Ministry of Education, Culture, Sports, Science and Technology, Japan, and by the Kansai Research Foundation for Technology Promotion. One of the authors, H. O., thanks research fund from Iketani Science and Technology Foundation.

References

[1] A. Fujishima, T.N. Rao and D.A. Tryk, J. Photochem. Photobiol. C: Photochem. Rev. 1 (2000) 1.
[2] M.R. Hoffman, S.T. Martin, W. Choi and D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
[3] S. Sato, Chem. Phys. Lett. 123 (1986) 126.
[4] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, Science 293 (2001) 269.
[5] T. Lindgren, J.M. Mwabora, E. Avendano, J. Jonsson, A. Hoel, C.-G. Granqvist and S.-E. Lindquist, J. Phys. Chem. B 107 (2003) 5709.
[6] H. Irie, Y. Watanabe and K. Hashimoto, J. Phys. Chem. B 107 (2003) 5483.
[7] K. Kobayakawa, Y. Murakami and Y. Sato, J. Photochem. Photobiol. A: Chem. 170 (2005) 177.
[8] Y. Suda, H. Kawasaki, T. Ueda and T. Ohshima, Thin Solid Films 453–454 (2004) 162.
[9] S. Yin, H. Yamaki, M. Komatsu, Q. Zhang, J. Wang, Q. Tang, F. Saito and T. Sato, J. Mater. Chem. 13 (2003) 2996.
[10] H. Ozaki, S. Iwamoto and M. Inoue, Chem. Lett. 34 (2005) 1082.
[11] W. Choi, A. Termin and M.R. Hoffman, J. Phys. Chem. 98 (1994) 13669.
[12] M.I. Litter and J.A. Navio, J. Photochem. Photobiol. A: Chem. 98 (1996) 171.
[13] K. Nagaveni, M.S. Hegde and G. Madras, J. Phys. Chem. B 108 (2004) 20204.
[14] T. Ohno, Z. Miyamoto, K. Nishijima, H. Kanemitsu and F. Xueyuan, Appl. Catal. A: Gen. 302 (2006) 62.
[15] S. Iwamoto, K. Saito, M. Inoue and K. Kagawa, Nano Lett. 1 (2001) 417.
[16] F. Amano, T. Yamaguchi and T. Tanaka, J. Phys. Chem. B 110 (2006) 281.
[17] X. Gao and I.E. Wachs, J. Phys. Chem. B 104 (2000) 1261.
[18] H. Yamashita, M. Harada, J. Misaka, M. Takeuchi, K. Ikeue and M. Anpo, J. Photochem. Photobiol. A: Chem. 148 (2002) 257.
[19] S. Klosek and D. Raftery, J. Phys. Chem. B 105 (2001) 2815.
[20] J.C.-S. Wu and C-H. Chen, J. Photochem. Photobiol. A: Chem. 163 (2004) 509.
[21] K. Iketani, R. Sun, M. Toki, K. Hirota and O. Yamaguchi, Mater. Sci. Eng. B 108 (2004) 187.
[22] Y. Nakaoka and Y. Nosaka, J. Photochem. Photobiol. A: Chem. 110 (1997) 299.
[23] R.F. Howe and M. Grätzel, J. Phys. Chem. 91 (1987) 3906.
[24] M. Grätzel and R.F. Howe, J. Phys Chem. 94 (1990) 2566.