

CHARACTERIZATION OF Ti/Si BINARY OXIDES PREPARED BY THE SOL-GEL METHOD AND THEIR PHOTOCATALYTIC PROPERTIES: THE HYDROGENATION AND HYDROGENOLYSIS OF CH₃CCH WITH H₂O

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Abstract—Titanium-silicon (Ti/Si) binary oxides having different Ti content were prepared by the sol-gel method and utilized as photocatalysts for the hydrogenation and hydrogenolysis of CH₃CCH with H₂O. The photocatalytic reactivity and selectivity of these catalysts were investigated as a function of the Ti content and it was found that the hydrogenolysis reaction (C₂H₆ formation) was predominant in regions of low Ti content, while the hydrogenation reaction (C₃H₆ formation) proceeded in regions of high Ti content. The in situ photoluminescence, diffuse reflectance absorption, FT-IR, XAFS (XANES and EXAFS), and XPS spectroscopic investigations of these Ti/Si binary oxides indicated that the titanium oxide species are highly dispersed in the SiO₂ matrices and exist in a tetrahedral coordination exhibiting a characteristic photoluminescence spectrum. The charge transfer excited state of the tetrahedrally coordinated titanium oxide species plays a significant role in the efficient photoreaction with a high selectivity for the hydrogenolysis of CH₃CCH to produce mainly C₂H₆ and CH₄, while the catalysts involving the aggregated octahedrally coordinated titanium oxide species show a high selectivity for the hydrogenation of CH₃CCH to produce C₃H₆, being similar to reactions of the powdered TiO₂ catalysts. The good parallel relationship between the yield of the photoluminescence and the specific photocatalytic reactivity of the Ti/Si binary oxides as a function of the Ti content clearly indicates that the high photocatalytic reactivity of the Ti/Si binary oxides having low Ti content is associated with the high reactivity of the charge transfer excited state of the isolated titanium oxide species in tetrahedral coordination, [Ti⁴⁺-O⁻].

Key words: Photocatalysis, Titanium Oxide, Sol-Gel Method, Ti/Si Binary Oxide, Hydrogenation of Alkyne

INTRODUCTION

Titanium oxide utilized in photocatalytic systems attracted a great deal of attention, especially for environmental applications. The photocatalytic effectiveness of titanium oxide can vary greatly with their physical properties [Anpo and Yamashita, 1996; Anpo and Yamashita, 1997]. Recently, we have shown that the "sol-gel method" is a fascinating way to design highly active photocatalysts [Moon et al., 1997; Negishi et al., 1993]. Using this technique, binary oxide catalysts can be prepared although the local structure of the active sites as well as the catalytic properties are dependent on the composition of the binary oxides. In fact, Anpo et al. have reported that the photocatalytic reactivities of the Ti/Si binary oxides prepared by the coprecipitation method are affected by changing the composition of the catalyst [Anpo et al., 1986]. Therefore, it is special interest to investigate the relationship between the local structure of the titanium oxide species and the photocatalytic reactivity of the Ti/Si binary oxides prepared by the sol-gel method as a function of the Ti content. However,

until now there have been no detailed investigations not only on the characterization of the catalysts at the molecular level but also on the role the local structure of the active sites plays on the photocatalytic reactivities of such Ti/Si binary oxide catalysts.

In the present study, we deal with the preparation and characterization of the highly active tetrahedral titanium oxide species embedded into transparent SiO₂ matrices by the sol-gel method and have clarified the relationship between the local structure of the titanium oxide species and the photocatalytic properties in the hydrogenation and hydrogenolysis of CH₃CCH with H₂O. In addition, the effects of the addition of Pt on the photocatalytic properties has been studied in order to obtain useful and important information required for the design and application of highly active and selective photocatalytic systems.

EXPERIMENTAL

Ti/Si binary oxides having different Ti contents were prepared by the sol-gel method from mixtures of tetraethylorthosilicate and titaniumisopropoxide. Ti/Si gels were obtained by keeping the mixture at room temperature for several

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days, washed with sufficient amounts of boiled water and then calcined in dry air at 725 K for 5 h. The Ti/Si binary oxides were crushed and sieved to 0.25-mm-size particles. Calcination of the Ti/Si xerogel samples was carried out in dry air at 725 K for 5 h to produce stable Ti/Si binary oxide catalysts. The Pt-loaded Ti/Si binary oxide catalyst (1.0 wt% as Pt metal) was prepared by impregnating the binary oxide with an aqueous solution of H_2PtCl_6 . Prior to spectroscopic measurements and photocatalytic reactions, the catalysts were treated with O_2 at 725 K for 2 h and then evacuated for 2 h at 475 K. In the case of Pt-loaded catalysts, the pretreated catalyst was heated in H_2 at 475 K for 2 h and finally evacuated at the same temperature. The catalyst (150 mg) was spread out evenly on the flat bottom of the quartz cell. UV irradiation of the catalyst in the presence of CH_3CCH (11 μmol) and gaseous H_2O (54 μmol) was carried out using a 75-W high-pressure Hg lamp through water and color filters ($\lambda > 290 \text{ nm}$) at 275 K. The reaction products collected in the gas phase were analyzed by gas chromatography [Anpo et al., 1997].

The photoluminescence spectra of the catalyst were measured at 77 K using a Shimadzu RF-5000 spectrofluorometer. The UV-Vis absorption spectra were measured at 295 K by a Shimadzu UV-2200A double-beam digital spectrophotometer equipped with conventional components of a reflectance spectrometer. FT-IR spectra were recorded at 295 K with a Shimadzu FTIR-8500 spectrophotometer. X-ray diffraction patterns of the catalysts were obtained with a Rigaku RDA- γ A X-ray diffractometer using $\text{Cu K}\alpha$ radiation with a Ni filter. The XPS spectra were measured at 295 K with a V.G. Scientific ESCASCOPE photoelectron spectrometer using $\text{Mg K}\alpha$ radiation. The XAFS spectra (XANES and EXAFS) of the catalysts were measured at the BL-7C facility of the Photon Factory at the National Laboratory for High-Energy Physics, Tsukuba. Si(111) double crystals were used to monochromatize the X-rays from the 2.5 GeV electron storage ring. The Ti K-edge absorption spectra were recorded in the transmission mode or fluorescence mode at 295 K. The normalized spectra were obtained by a procedure described in previous literature [Yamashita et al., 1996] and Fourier transformation was performed on k^3 -weighted EXAFS oscillations in the range of 3–10 \AA^{-1} .

RESULTS AND DISCUSSION

The crystalline structures of Ti/Si binary oxides having different Ti contents were investigated by XRD measurements and these XRD patterns are shown in Fig. 1. The XRD patterns of the binary oxides exhibit only diffraction lines which are attributed to the crystalline anatase phase of TiO_2 . The very weak diffraction line assigned to the crystalline brookite phase of TiO_2 could be observed only with TS-100 sample. When the Ti content is decreased, these X-ray diffraction lines decrease in intensity and finally disappear. This indicates that in the Ti/Si binary oxides, the crystallinity of the titanium oxide species decreases when the Ti content is decreased.

In the FT-IR spectra of the Ti/Si binary oxides, a peak assigned to the Ti-O-Si bonding was observed at around 950 cm^{-1} indicating that the titanium oxide species were embed-

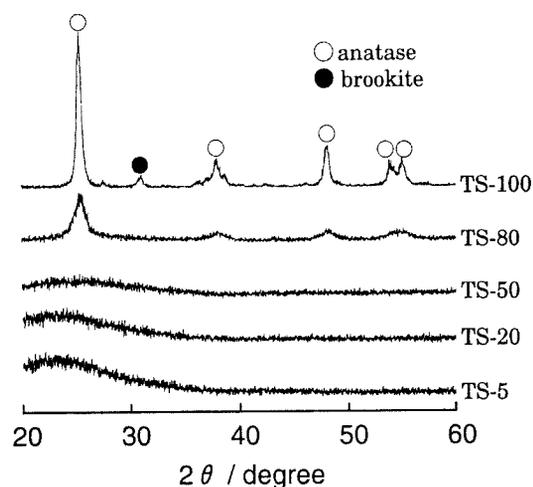


Fig. 1. X-ray diffraction patterns of Ti/Si binary oxides. Ti/Si binary oxides having a Ti content of 5–80 wt% as TiO_2 are referred as to TS-5–TS-80, respectively, and TS-100 sample is TiO_2 prepared by the gol-gel method.

ded into the SiO_2 matrices [Cambor et al., 1993]. Ti/Si binary oxides with lower TiO_2 content showed a remarkable shift in the Ti_{2p} XPS peak to higher binding energy levels, indicating that the particle size of the titanium oxide species decreases accompanied by local structural changes.

Fig. 2 shows the absorption spectra of Ti/Si binary oxides measured by the UV-Vis diffuse reflectance method. It can be seen that a decrease in the Ti content causes a remarkable shift in the absorption band towards shorter wavelength regions. Absorption spectra of the Ti/Si binary oxides with low Ti content exhibit a large shift towards shorter wavelength regions. This large shift is attributed to the size quantization effect arising from the presence of extremely small titanium oxide particles and/or the presence of highly dispersed titanium oxide species having a low coordination number. These results obtained by XRD, XPS and UV-Vis absorption meas-

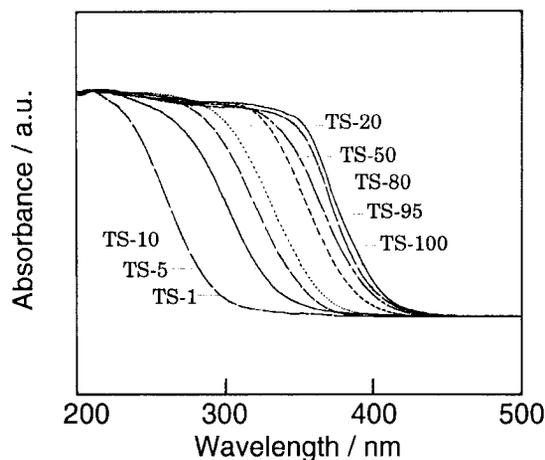


Fig. 2. Absorption spectra of Ti/Si binary oxides measured by the UV-Vis diffuse reflectance method. TS-1–TS-95 samples are the Ti/Si binary oxides of 1–95 wt% as TiO_2 , respectively, and TS-100 sample is TiO_2 prepared by the sol-gel method.

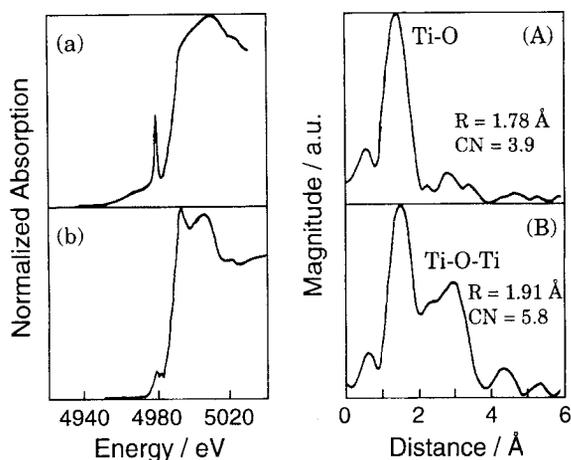


Fig. 3. XANES (left) and Fourier transforms of EXAFS spectra (FT-EXAFS) (right) of Ti/Si binary oxides. Ti contents are (a) 1 wt% (TS-1) and (b) 80 wt% (TS-80) as TiO₂, respectively.

Measurements clearly show that a decrease in the Ti content changes the crystalline structure of the titanium oxides from aggregates in an anatase phase to ultrafine titanium oxide species with an amorphous structure and eventually to isolated titanium oxide species having a local coordinate geometry different from those of the crystalline anatase titanium oxide.

Fig. 3 shows the XANES spectra of Ti/Si binary oxides. Ti/Si binary oxides with lower TiO₂ content (<20 wt% TiO₂) exhibit an intense single preedge peak, indicating that the titanium oxide species have a tetrahedral coordination in the SiO₂ matrices [Yamashita et al., 1996]. On the other hand, the Ti/Si binary oxide having a large Ti content of 80% as TiO₂ (TS-80) exhibits three characteristic weak preedge peaks, indicating the presence of the crystalline anatase TiO₂.

Fig. 3 also shows the Fourier transforms of EXAFS spectra (FT-EXAFS) of the catalysts (all data are given without corrections for phase shifts). All of the catalysts investigated in the present study exhibit a strong peak at around 1.6 Å which can be assigned to the neighboring oxygen atoms (Ti-O). The Ti/Si binary oxides having low Ti content exhibit only Ti-O peaks, indicating the presence of the isolated titanium oxide species on these catalysts. From the results obtained by the curve-fitting analysis of the EXAFS spectra, it was found that the Ti/Si binary oxides having low Ti content consists of 4-coordinate titanium oxide species. As shown in Fig. 3, the Ti/Si binary oxide having a large Ti content (TS-80) exhibits an intense peak at around 2.7 Å assignable to the neighboring titanium atoms behind the oxygen (Ti-O-Ti), indicating the aggregation of the titanium oxide species in these catalysts. These XANES and FT-EXAFS investigations indicate that the Ti/Si binary oxides having a low Ti content involve only the well-isolated tetrahedral titanium oxide species, while the Ti/Si binary oxides having a large Ti content involve the aggregated octahedral titanium oxide species.

Fig. 4 shows the surface Ti composition of Ti/Si binary oxides calculated from the ratio of the Ti(2p_{3/2}) to Si(2p_{1/2}) XPS band intensities. It can clearly be seen that there is a steady decrease in the surface Ti composition as the bulk Ti

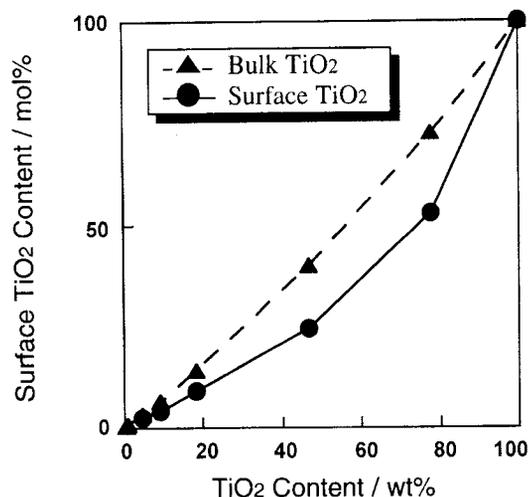


Fig. 4. The surface Ti composition of Ti/Si binary oxides calculated from the signal intensity of Ti (2p_{3/2}) and Si (2p_{1/2}) XPS bands in the Ti/Si binary oxides. A bold line: the surface Ti composition calculated from the results of XPS measurement. A dotted line: the original composition of the sols (bulk TiO₂ content).

content in the Ti/Si binary oxides decreases. However, the surface Ti composition is much smaller than what can be expected from the original composition of the sols in the region of middle Ti content of around 50 wt% as TiO₂, suggesting the segregation of SiO₂ in the surface region of the binary oxides.

As shown in Fig. 5, the Ti/Si binary oxides having low Ti content of less than 20 wt% as TiO₂ exhibit the characteristic photoluminescence spectra at around 490 nm upon excitation at around 280 nm at 77 K. The observed photolu-

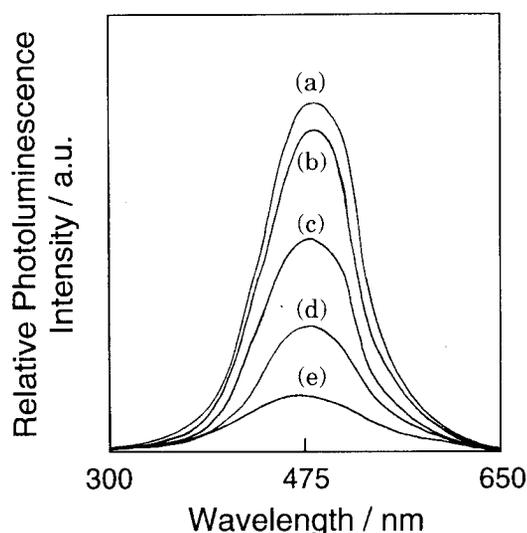


Fig. 5. Photoluminescence spectrum of the Ti/Si binary oxide (TS-5) (a), and the effects of the addition of CH₃CCH and H₂O (b-e) on the photoluminescence spectrum. Measured at 77 K, excitation at 290 nm, pressure of added CH₃CCH: b) 2, d) 20 Torr, and H₂O: c) 0.5, e) 10 Torr.

miescence spectra are in good agreement with those of highly dispersed tetrahedrally coordinated titanium oxides anchored onto Vycor glass where the absorption of UV light at around 280 nm brought about an electron transfer from the lattice oxygen (O_i^{2-}) to the titanium ion (Ti^{4+}) to form a charge transfer excited state, $(Ti^{3+}-O^-)^*$ [Anpo and Chiba, 1992; Yamashita et al., 1996]. These findings clearly show the presence of highly dispersed titanium oxide species in the oxides having a tetrahedral coordination. When the Ti content is decreased, the intensity of photoluminescence increased gradually in the region of low Ti content less than 20 wt% as TiO_2 , indicating that in the Ti/Si binary oxides the dispersion of the titanium oxide species increased when the Ti content is decreased. On the other hand, Ti/Si binary oxides having a large Ti concentration did not exhibit any photoluminescence.

As shown in Fig. 5, the addition of H_2O or CH_3CCH molecules onto the Ti/Si binary oxides leads to an efficient quenching of the photoluminescence and shortening of its lifetime, their extent depending on the amount of added gasses. Such an efficient quenching of the photoluminescence with H_2O or CH_3CCH indicates that added CH_3CCH or H_2O interacts and/or reacts with the titanium oxide species in the excited state.

UV irradiation of the Ti/Si binary oxides in a gaseous mixture of CH_3CCH and H_2O led to the hydrogenolysis reaction accompanied by a $C\equiv C$ bond fission to produce CH_4 and C_2H_6 as well as hydrogenation without the $C\equiv C$ bond fission to form C_3H_6 as the main products. As shown in Fig. 6, the hydrogenolysis reaction (C_2H_6 formation) is predominant in regions of low Ti content, while the hydrogenation reaction (C_3H_6 formation) also proceeds efficiently in regions of high Ti content. As described previous literature [Anpo, 1989], the hydrogenolysis reaction is attributed to the close existence of the photoformed electron and hole, i.e., the $Ti^{3+}-O^-$ pair species. The charge transfer excited state of the isolated tetrahedral titanium oxide species formed in the Ti/Si binary

oxides having low Ti content plays a significant role as the reactive species which lead the efficient hydrogenolysis reaction. On the other hand, the Ti/Si binary oxides having high Ti content contain the aggregated TiO_2 fine particle on which the photocatalytic reactions in the same manner as on bulk TiO_2 catalysts become predominant and the reduction reaction by electrons and the oxidation reaction by holes occur separately from each other on different sites, leading to the selective formation of C_3H_6 (hydrogenation reaction). In Fig. 6, an increase in photocatalytic activity of the titanium oxide species in regions of low Ti content as well as an increase in regions of high Ti content can also be observed. The specific photocatalytic activity of the titanium oxide species (normalized by unit weight of the titanium oxide) in the binary oxides with low Ti content was found to be higher than that of the Degussa P-25 anatase TiO_2 . These findings indicate that the Ti/Si binary oxides prepared by the sol-gel method are useful and promising as a photocatalyst. Furthermore, in regions of low Ti content, there was a good parallel between the photocatalytic activity of the titanium oxide species and the yield of the photoluminescence of the Ti/Si binary oxides, suggesting that the appearance of such high photocatalytic activity is closely associated to the formation of the charge transfer excited complex, i.e., the $Ti^{3+}-O^-$ pair, of the highly dispersed tetrahedral titanium oxide species.

The effect of Pt-loading on the photocatalytic reactivity of Ti/Si binary oxides has also been investigated. Although the addition of Pt onto the Ti/Si binary oxides is effective in an increase in the photocatalytic reactivity, only the formation of C_3H_6 (hydrogenation reaction) is promoted, accompanied by a decrease in the formation of C_2H_6 (hydrogenolysis reaction) independently on the Ti content of binary oxides. Pt-loading onto the Ti/Si binary oxide having a low Ti content led to an efficient quenching of the photoluminescence, accompanied by the shortening of its lifetime. Because the results obtained by EXAFS and absorption measurements indicated that the local structure of the Ti/Si binary oxide having a low Ti content was not altered by the Pt-loading, the effective quenching of the photoluminescence can be attributed to the electron transfer from the photo-excited titanium oxide species to Pt metals. As a result, on the Pt-loaded the Ti/Si binary oxide having a low Ti content, photocatalytic reactions which proceed in the same manner as on bulk TiO_2 become predominant, meaning that the reduction reaction by electrons and the oxidation reaction by holes occurring separately from each other on different sites becomes predominant, leading to the selective formation of C_3H_6 (hydrogenation reaction).

CONCLUSIONS

Ti/Si binary oxides having different Ti content were prepared using the sol-gel method and used as photocatalysts for the hydrogenation and hydrogenolysis of CH_3CCH with H_2O . The photocatalytic hydrogenolysis reaction (C_2H_6 formation) was found to be predominant in regions of low Ti content, while the hydrogenation reaction (C_3H_6 formation) proceeded in regions of high Ti content. In Ti/Si binary oxides hav-

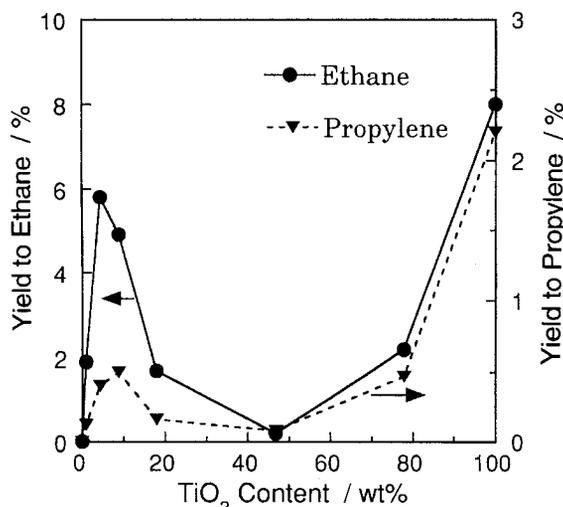


Fig. 6. The effects of Ti content on the photocatalytic activities of Ti/Si binary oxides for the hydrogenation (C_3H_6 formation) and hydrogenolysis (C_2H_6 formation) of CH_3CCH with H_2O . The yields obtained after photoreaction for 2 h.

ing lower Ti content the isolated titanium oxide species in tetrahedral coordination were found to exist in the SiO₂ matrices. These titanium oxide species exhibited a characteristic photoluminescence spectrum attributed to the radiative decay from the charge transfer excited state of these species and promoted a high specific photocatalytic reactivity. The good parallel between the yield of the photoluminescence and the yield of the photocatalytic reaction obtained clearly indicated that the charge transfer excited state of the titanium oxide species in a tetrahedral coordination plays a significant role in the photocatalytic reaction, especially for the hydrogenolysis reaction. The present study clearly demonstrates that Ti/Si binary oxides prepared by the sol-gel method are promising candidates as new and efficient photocatalysts and the control of the charge separation is important in developing highly efficient and selective photocatalysts.

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