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Characterization of Titanium−Silicon Binary Oxide Catalysts Prepared by the Sol−Gel Method and Their Photocatalytic Reactivity for the Liquid-Phase Oxidation of 1-Octanol

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Titanium−silicon (Ti/Si) binary oxides having different Ti contents were prepared by the sol−gel method and used as photocatalysts. The photocatalytic reactivity of these catalysts was investigated as a function of the Ti content for the liquid-phase oxidation of 1-octanol to 1-octanal, and it was found to be dramatically enhanced in regions of lower Ti content. In situ photoluminescence, UV−vis reflectance, FT-IR, ESR, XAFS, XRD, and XPS spectroscopic investigations of these Ti/Si binary oxides indicated that the titanium oxide species are highly dispersed in the SiO_2 matrixes and exist in a tetrahedral coordination exhibiting a characteristic photoluminescence spectrum due to the radiative decay from the charge-transfer excited state of the tetrahedrally coordinated titanium oxide species. 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 a low Ti content is associated with the high reactivity of the charge-transfer excited state of the isolated titanium oxide species in tetrahedral coordination, $[Ti^{3+}-O^{-}]^*$.

Introduction

Titanium oxide catalysts have attracted a great deal of attention as potential photocatalysts to address urgent and global environmental concerns.[1−4] The photocatalytic degradation of various toxic compounds in aqueous solutions using fine titanium oxide particles has been studied by many researchers.[5−10] However, to avoid the filtration and suspension of small particle photocatalysts, the design of highly efficient and transparent titanium oxide photocatalysts is strongly desired. The preparation of titanium oxide catalysts on transparent supports such as Vycor glass by anchoring or embedding methods can be considered one of the most promising ways to achieve such applicable photocatalysts.[10]

Anpo et al. have reported that titanium oxides having a tetrahedral coordination can be chemically supported onto transparent Vycor glass by the chemical vapor deposition or anchoring method and have shown that such catalysts exhibit high and characteristic photocatalytic reactivities.[11−13] Recently, highly dispersed titanium oxides included within the zeolite cavities and framework have been prepared as tetrahedral titanium oxide species using an ion-exchange method or hydrothermal synthesis and used as efficient photocatalysts for various photocatalytic reactions such as the decomposition of NO_x into N_2 and O_2.[14−16] These findings clearly suggest that highly dispersed tetrahedral titanium oxide catalysts exhibit unique and efficient reactivity for various gas-phase photocatalytic reactions compared to bulk TiO_2 powder catalysts.

The sol−gel process is expected to offer unique advantages for the preparation of such highly dispersed tetrahedrally coordinated and transparent photocatalysts, especially to be applied for coating material, active thin-film photocatalysts, and multicomponent ceramics.[17−19] For binary oxide catalysts, the local structure of the active sites as well as the catalytic and photocatalytic properties are strongly dependent on the composition of the oxides.[19] Therefore, it is of 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. 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.[20] Imamura et al. have reported that the Ti/Si binary oxides prepared by the sol−gel method exhibit a high catalytic activity for the selective epoxidation of alkenes[21] while Davis et al. have investigated the local structure of the titanium oxide species in the Ti/Si binary oxide using XAFS techniques.[22,23] 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 of highly active tetrahedral titanium oxide species embedded into transparent SiO_2 matrixes using the sol−gel method and have carried out a comprehensive characterization of these catalysts by means

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of in situ photoluminescence, UV−vis reflectance, FT-IR, ESR, XAFS, XPS, and XRD spectroscopic techniques. These Ti/Si binary oxide catalysts have also been successfully applied as photocatalysts for the liquid-phase oxidation of 1-octanol to produce 1-octanal at 300 K in an acetonitrile solution. Special attention has been focused on the relationship between the local structure of the titanium oxide species in the Ti/Si binary oxides and the photocatalytic reactivity in order to provide vital information for the design and application of such highly efficient photocatalytic systems in the degradation of toxic compounds diluted in a liquid phase.

Experimental Section

Catalysts. Tetraethyl orthosilicate (TEOS, 99%), titanium isopropoxide (TPOT, 99%), and ethanol (99.5%) were supplied by Kishida Chemicals, Japan, and used as received. Titanium−silicon (Ti/Si) binary oxides having different Ti contents were prepared by the sol−gel method from ethanol solutions of mixtures of tetraethyl orthosilicate (TEOS) and titanium isopropoxide (TPOT). These starting ethanol solutions were prepared from ethanol (20 mL) and the mixtures (20 mL) of TEOS and TPOT. These solutions were kept in a sealed container under the air of the saturated moisture which was kept in the storage room controlled at the room temperature of 296 ± 1 K. Thus, the gelation of mixtures of TEOS and TPOT in ethanol solution was carried out under mild conditions using the saturated moisture (21 ± 2 mmHg) of the air at 296 ± 1 K without the addition of any other reagents. The gelation proceeded slowly and was completed within 7−15 days, forming the homogeneous Ti/Si gel samples. The period required for the complete gelation depended on the composition of the starting mixtures. Aging and drying of the gel samples leading to the transformation from gel to xerogel were carried out by allowing the samples to stand under the same conditions for an extra 4 weeks. These xerogel samples were transparent and seemed to have a homogeneous composition without any segregation. The Ti/Si xerogels formed in this way were crushed and sieved to 0.25 mm size particles and washed with sufficient amounts of boiled water. 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. Prior to the spectroscopic measurements and photocatalytic reactions, these binary oxide catalysts were treated with oxygen at 725 K for 2 h and evacuated at 475 K for 2 h to remove any organic contaminants adsorbed on the catalysts to obtain clean surfaces and the reproducible photocatalytic properties.

Characterization. The photoluminescence spectra of the catalyst were measured at 77 K using a Shimadzu RF-5000 spectrophotofluorometer. 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. The FT-IR spectra were recorded at 295 K with a Shimadzu FTIR-8500 spectrophotometer using the sample wafers of mixture of the catalyst and KBr. X-ray diffraction patterns of the catalysts were obtained with a Rigaku RDA-γA X-ray diffractometer using Cu Kα radiation with a Ni filter. ESR spectra were recorded at 77 K using a JEOL JES-RE2X spectrometer operating in the X-band mode. The XPS spectra were measured at 295 K with a V.G. Scientific ESCASCOPE photoelectron spectrometer using Mg Kα 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,[24] and Fourier transformation was performed on k^3-weighted EXAFS oscillations in the range 3−10 Å^{-1}. The curve-fitting of the EXAFS data was carried out by employing the iterative nonlinear least-squares method and the empirical backscattering parameter sets extracted from the shell features of titanium compounds.

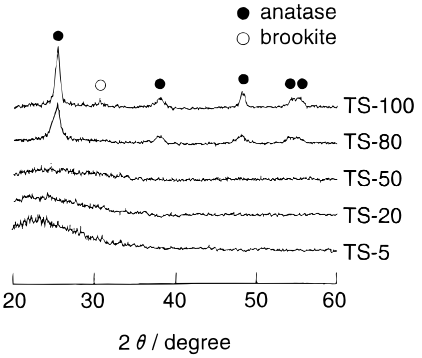

Figure 1. X-ray diffraction patterns of Ti/Si binary oxides. Ti/Si binary oxides having a Ti content of 5 and 80 wt % TiO_2 are referred to as TS-5 and TS-80, respectively, and the TS-100 sample is TiO_2 prepared by the sol−gel method.

Photocatalytic Reaction. The catalyst (50 mg) was preheated in dry air at 725 K and cooled to room temperature before being placed with 1-octanol (0.5 mmol) in a volumetric flask (25 mL) which was then filled with acetonitrile. The sample was then transferred to a quartz test tube (30 mm i.d.) and sealed with a rubber septum. Oxygen was bubbled through a Teflon tube (1 mm i.d.), and the sample was irradiated at 300 K with vigorous and continuous stirring in a Rayonet photochemical reactor (Southern New England Ultraviolet).[13] A phosphor-coated low-pressure mercury lamp, RPR-3000 (blazed at about 300 nm), was used as the excitation source. The products were analyzed on a Hewlett-Packard model 5890 gas chromatograph equipped with an Alltech capillary column (0.25 mm × 25 m).

Results and Discussion

The crystalline structures of Ti/Si binary oxides having different Ti contents were investigated by XRD measurements. The XRD patterns obtained are shown in Figure 1. The XRD patterns of the binary oxides exhibit only diffraction lines which are attributed to the crystalline anatase phase of TiO_2. The sizes of the crystallites measured by peak half-width were 115 and 67 Å with the TS-100 and TS-80 samples, respectively. 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. Especially, in the binary oxides having Ti contents lower than 50 wt % TiO_2, the titanium oxide species are present in amorphous structure within the SiO_2 matrixes.

Figure 2 shows the FT-IR spectra of Ti/Si binary oxides having different Ti contents. With these oxides, three characteristic bands can be observed at around 1100, 950, and 650 cm^{-1}.[22,23] SiO_2 and the Ti/Si binary oxide having a low Ti content exhibit a band at around 1100 cm^{-1} which can be assigned to the stretching of the Si−O−Si bond in the tetrahedral

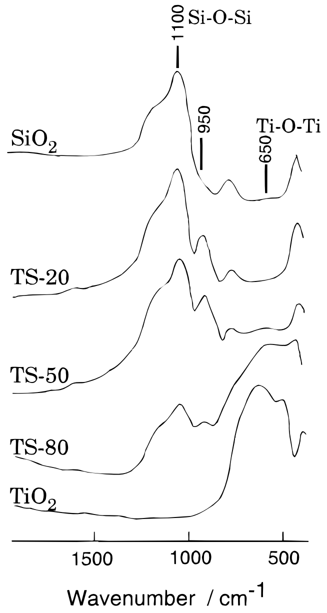

Figure 2. FT-IR spectra of Ti/Si binary oxides and powdered SiO_2 and TiO_2 (anatase). TS-20, TS-50, and TS-80 samples are the Ti/Si binary oxides of 20, 50, and 80 wt % TiO_2, respectively.

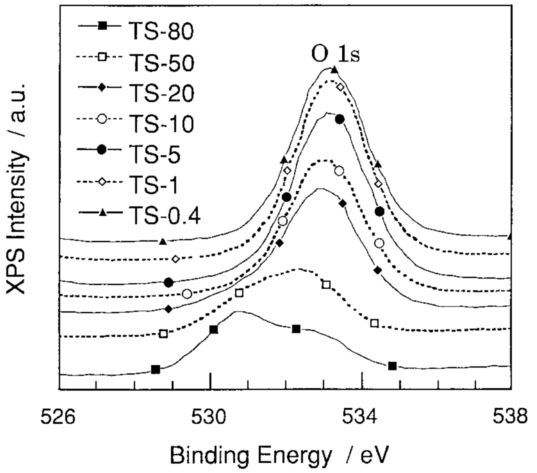

Figure 3. X-ray photoelectron spectra of the O 1s level for Ti/Si binary oxides. TS-0.4−TS-80 samples are the Ti/Si binary oxides of 0.4−80 wt % TiO_2, respectively.

SiO_4 unit of the SiO_2 matrixes. TiO_2 and the Ti/Si binary oxide having a large Ti content exhibit a band at around 650 cm^{-1} which is representative of TiO_2 matrixes, while the Ti/Si binary oxides exhibit an additional band at around 950 cm^{-1}. This band has been assigned to the stretching of the Si−O^- species of Si−O−Ti or Si−O^- defect sites which are formed by the inclusion of Ti^{4+} ions into the SiO_2 matrixes in the previous literature.[23,25] Thus, the appearance of the band at around 950 cm^{-1} indicates that the titanium oxide species are embedded into SiO_2 matrixes within these Ti/Si binary oxides.

The XPS spectra of the catalysts were measured in order to obtain information on the binding energy of the titanium oxide species. Figure 3 shows the XPS spectra of the O 1s band for Ti/Si binary oxides having different Ti contents. The band of the O ion in the TiO_2 matrixes (Ti−O−Ti) can be observed at around 530.5 eV, and that of the SiO_2 matrixes (Si−O−Si) can be observed at around 533.5 eV. With an increase in the Ti content of these Ti/Si binary oxides, the O 1s peak shifts from 533.5 eV to a lower energy of around 532.5 eV. Stakheev and co-workers observed the same shift of the O 1s band with a change in the Ti content of the Ti/Si binary oxides prepared by coprecipitation and concluded that this shift reflects a substitution of the Si atoms by less electronegative and more polarizable Ti atoms in the SiO_2 matrixes.[26] With the Ti/Si binary oxide having a Ti content of 50−80 wt % (TS-50, TS-80), the two O 1s bands can be observed at around 530.5 and 532.5 eV. Considering the previous detailed XPS study on Ti/Si binary oxides,[25] the appearance of these two bands indicates the formation of a two-phase system containing both a titania-rich phase and a phase in which the titanium oxide species are embedded into the SiO_2 matrixes, these results being in good agreement with the results of the FT-IR investigations.

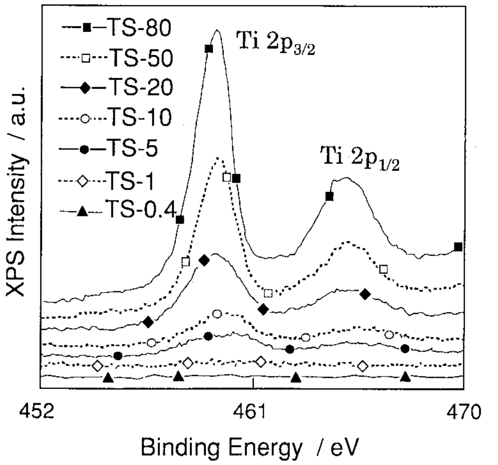

Figure 4. X-ray photoelectron spectra of the Ti 2p levels for Ti/Si binary oxides. TS-0.4−TS-80 samples are Ti/Si binary oxides of 0.4−80 wt % TiO_2, respectively.

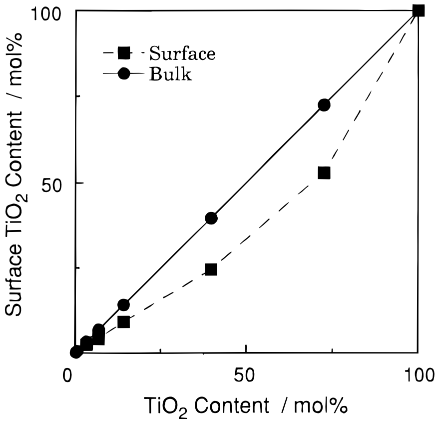

Figure 5. Surface Ti composition of Ti/Si binary oxides calculated from the signal intensity of $Ti(2p_{3/2})$ and $Si(2p_{1/2})$ XPS bands in the Ti/Si binary oxides. Dotted line: the surface Ti composition calculated from the results of XPS measurement. Bold line: the original composition of the sols (bulk Ti content).

Figure 4 shows the XPS spectra of the Ti 2p band for Ti/Si binary oxides having different Ti contents. The binding energy of the $Ti(2p_{3/2})$ and $Ti(2p_{1/2})$ bands shifts to higher values when the Ti content decreases, especially with binary oxides having less than 20 wt % TiO_2. A similar tendency has been observed for the $Ti(2p_{3/2})$ XPS signals of the Ti/Si and Ti/Al binary oxides prepared by coprecipitation.[20,27] Taking these results into consideration, such a shift in the binding energy of the Ti 2p bands to higher values can be attributed to the smaller relaxation energy for the highly dispersed titanium oxide species as compared to the powdered bulk TiO_2 catalysts.

Figure 5 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

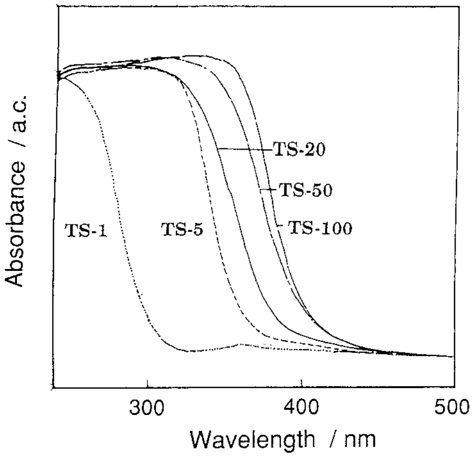

Figure 6. Absorption spectra of Ti/Si binary oxides measured by the UV−vis diffuse reflectance method. TS-1−TS-50 samples are the Ti/Si binary oxides of 1−50 wt % TiO_2, respectively, and the TS-100 sample is TiO_2 prepared by the sol−gel method.

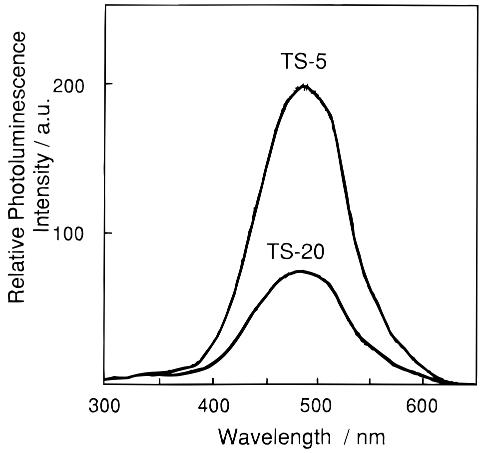

Figure 7. Photoluminescence spectra of Ti/Si binary oxides. TS-5 and TS-20 samples are the Ti/Si binary oxides of 5 and 20 wt % TiO_2, respectively. Photoluminescence spectra were measured at 77 K by the excitation at 280 nm.

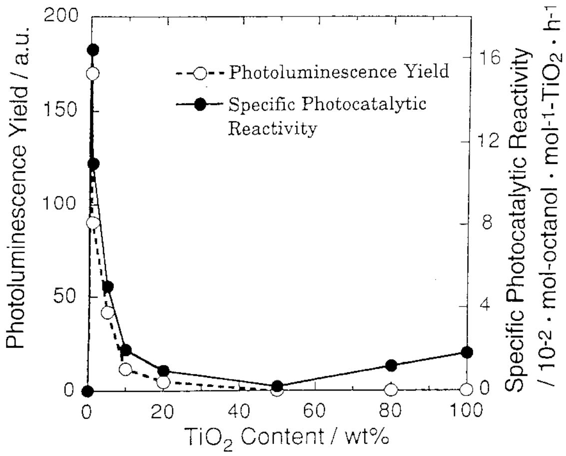

Figure 8. Specific intensity of the photoluminescence of Ti/Si binary oxides and their specific photocatalytic reactivities for the liquid-phase oxidation of 1-octanol to 1-octanal.

decrease in the surface Ti composition as the bulk Ti 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 % TiO_2, suggesting the segregation of SiO_2 in the surface region of the binary oxides.

Figure 6 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 toward shorter wavelength regions. Similar studies were carried out on the Ti/Si and Ti/Al binary oxides having various compositions of Ti:Si and Ti:Al prepared by coprecipitation, and a considerable shift toward shorter wavelength regions was observed for the absorption band of the highly dispersed titanium oxide species.[20,27] It can be said that such a large shift toward shorter wavelengths for the Ti/Si binary oxides with low Ti content 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 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, the extent of the transformation strongly depending on the Ti content.

Ti/Si binary oxides having a low Ti content of less than 20 wt % TiO_2 exhibited the characteristic photoluminescence spectra at around 490 nm when the catalysts were excited at around 280 nm. Figure 7 shows the typical photoluminescence spectra observed with Ti/Si binary oxides having a low Ti content by excitation at around 280 nm at 77 K. The observed photoluminescence spectra are in good agreement with those of the 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_l^{2-}) to the titanium ion (Ti_l^{4+}) to form a charge-transfer excited state, $(Ti^{3+}-O^{-})^*$.[12−15] These findings show that the observed photoluminescence spectrum is attributed to the radiative decay process from the thus formed charge-transfer excited state to the ground state of the highly dispersed titanium oxide species having a tetrahedral coordination. On the other hand, Ti/Si binary oxides having a large Ti concentration did not exhibit any photoluminescence.

Figure 8 shows the effect of the Ti content on the yield of the photoluminescence spectrum due to the presence of highly dispersed titanium oxide species in the Ti/Si binary oxides. Decreasing the Ti content led to an increase in the yield of the photoluminescence spectrum. At the same time, the band position shifted to the shorter wavelength regions. These findings indicate that such a decrease in the Ti content of the binary oxides causes the titanium oxide species to exist in a highly dispersed state with a low coordination in the SiO_2 matrixes. Similar phenomena can be observed for the Zr/Si binary oxide catalysts prepared by the sol−gel method in which a decrease in the Zr content caused the photoluminescence intensity to increase and its band position to shift to shorter wavelength regions, indicating that zirconium oxide species are highly dispersed in a state of coordinative unsaturation within the Zr/Si binary oxides.[19]

Figure 9 shows the XANES spectra of Ti/Si binary oxides. The XANES spectra of the titanium oxide catalyst at the Ti K-edge show several well-defined preedge peaks which are related to the local structures surrounding the Ti atom, while the relative intensities of the preedge peaks also provide useful information on the coordination number.[22,28−31]

Ti/Si binary oxides having a low Ti content (TS-1, TS-5) exhibit an intense single preedge peak, indicating that the

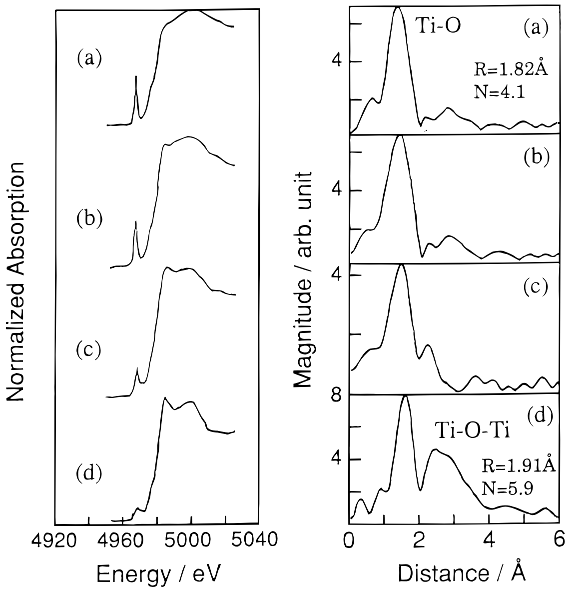

Figure 9. XANES (left) and Fourier transforms of EXAFS spectra (FT-EXAFS) (right) of Ti/Si binary oxides. Ti contents are (a) 1 wt % (TS-1), (b) 5 wt % (TS-5), (c) 20 wt % (TS-20), and (d) 80 wt % (TS-80) TiO_2, respectively.

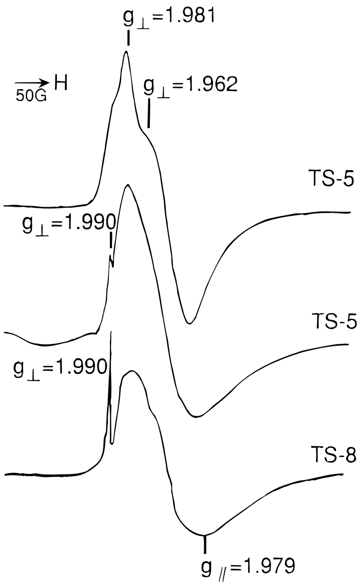

Figure 10. ESR spectra of the Ti^{3+} ions generated by the photoreduction of Ti/Si binary oxides with H_2 at 77 K. ESR signal was also recorded at 77 K. TS-5, TS-50, and TS-80 samples are the Ti/Si binary oxides of 5, 50, and 80 wt % TiO_2, respectively.

titanium oxide species have a tetrahedral coordination in the SiO_2 matrixes. The tetrahedrally coordinated Ti such as $Ti(OPr^i)_4$ are known to exhibit an intense single preedge peak due to the lack of an inversion center in the regular tetrahedron structure. As can be seen in Figure 9, for the Ti/Si binary oxide having a high Ti content of 20 wt % TiO_2 (TS-20), the single characteristic preedge peak is rather weak, indicating that the catalyst consists of a mixture of tetrahedrally and octahedrally coordinated titanium oxide species. On the other hand, the Ti/Si binary oxide having a large Ti content of 80% as TiO_2 (TS-80) exhibits three characteristic weak preedge peaks. Because these characteristic small preedge peaks can be attributed to the transitions from the 1s core level of Ti to three different kinds of molecular orbitals ($1t_{1g}$, $2t_{2g}$, and $3e_g$) of anatase TiO_2, these observations indicate the presence of the crystalline anatase TiO_2, being in good agreement with the results of XRD analysis.

Figure 9 also shows the Fourier transforms of EXAFS spectra (FT-EXAFS) of the catalysts, and 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 contents of 1 and 5 wt % TiO_2 (TS-1, TS-5) 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 (*R* factor of the accuracy of the curve fitting: 9.0%) of the EXAFS spectra, as can be seen in Figure 9, it was found that the Ti/Si binary oxide having the lowest Ti content (TS-1) consists of 4-coordinate titanium ions with a coordination number (*N*) of 4.1 ± 0.5 and an atomic distance (*R*) of 1.82 ± 0.02 Å. This atomic distance is similar to those observed with tetrahedrally coordinated titanium oxide which is anchored onto Vycor glass by the CVD method.[13] It should be mentioned that an atomic distance of the Ti−O bond of the highly dispersed tetrahedrally coordinated titanium oxide species is shorter by 0.14 Å than that of the bulk TiO_2 of 1.96 Å.[14]

As shown in Figure 9, the Ti/Si binary oxide having a large Ti content (TS-80) exhibits an intense peak at around 2.7 Å. This peak can be assigned to the neighboring titanium atoms behind the oxygen (Ti−O−Ti), indicating the aggregation of the titanium oxide species in these catalysts.[14,15] Results of the coordination number (*N*) of 5.9 ± 0.5 and an atomic distance (*R*) of 1.91 ± 0.02 Å for the Ti/Si binary oxide having a large Ti content (TS-80) obtained by the curve-fitting analysis (*R* factor of the accuracy of the curve fitting: 8.2%) of the EXAFS spectra suggest the presence of an aggregated octahedral titanium oxide species with this catalyst.

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 whose local structure is maintained in the regions having the Ti content of less than 20 wt % TiO_2, while the Ti/Si binary oxides having a large Ti content involve the aggregated octahedral titanium oxide species (anatase TiO_2 phase).

To investigate the local structure of the titanium oxide species in Ti/Si binary oxide catalysts, an ESR technique was incorporated to monitor the Ti^{3+} ions which were formed by the photoreduction of the oxide with H_2 at 77 K (1), maintaining the coordination geometry of the original Ti^{4+} species.[14,32]

$$(\mathrm{Ti}^{4+}{-}\mathrm{O}^{2-}) + \mathrm{H}_2 \rightarrow (\mathrm{Ti}^{3+}{-}\mathrm{OH}^{-}) + \mathrm{H} \tag{1}$$

As shown in Figure 10, the ESR spectrum of the Ti^{3+} ions formed in this way in the Ti/Si binary oxide having a low Ti content of 5 wt % TiO_2 (TS-5) shows two different types of Ti^{3+} signals with *g* values of $g_\perp = 1.981$ and 1.962. The addition of H_2O onto the sample led to a decrease in the intensity of the ESR signal with a value of $g_\perp = 1.981$, the extent depending on the amount of H_2O added. Furthermore, the addition of excess amounts of H_2O led to a complete disappearance of the signal. Simultaneously, the addition of H_2O also led to an increase in the intensity of the ESR signal with a value of $g_\perp = 1.962$. From the *g* value of $g_\perp = 1.981$ and the characteristic shape of the spectrum as well as the spectrum changes by the addition of H_2O, it can be concluded that the Ti^{3+} species are present in a tetrahedral coordination and that the original Ti^{4+} oxide species were also present in a tetrahedral coordination, since the photoreduction of the oxide at 77 K did not modify the coordination structure of the Ti^{4+} ions.[14,32] The ESR signal with a *g* value of 1.962 can be assigned as the coordinatively saturated Ti^{3+} species having H_2O or OH^- as ligands. These H_2O or OH^- species are formed by the processes of the photoreduction of Ti^{4+} ions by H_2 at 77 K. On the other hand, the Ti/Si binary oxide having a large Ti content (TS-80) exhibits an intense and sharp ESR signal with a value of $g_{\perp} = 1.990$. This characteristic ESR signal indicates the presence of the aggregated octahedral titanium oxide species.[32]

UV irradiation of the Ti/Si binary oxides in the 1-octanol−acetonitrile solution in the presence of O_2 led to the photocatalytic oxidation of 1-octanol to 1-octanal as the major reaction. The selectivity for the formation of 1-octanal at the initial stage of the reaction was >95% on the binary oxides having Ti content lower than 20 wt % TiO_2. No products could be detected in the dark under these same reaction conditions. Figure 8 shows the specific photocatalytic reactivities of the catalysts per unit weight of TiO_2. A remarkable increase in the specific photocatalytic reactivity of the catalysts can be seen for the catalysts having a low Ti content while a slight increase can be seen for the catalysts having a high Ti content. The specific photocatalytic reactivity of these binary oxides having Ti content of 0.4−5 wt % TiO_2 was found to be much higher than that of the "standard TiO_2 catalyst", anatase TiO_2 (Degussa P-25). The quantum yields determined with the binary oxide at 1 wt % TiO_2 under the UV irradiation ($\lambda = 300$ nm) of light flux of 1×10^{17}/min cm^3 was 22%, while it was 12% for TiO_2 (P-25) and 4% for TiO_2 powder prepared by the same sol−gel method. These findings indicate that Ti/Si binary oxides, especially the oxides having a low Ti content prepared by the sol−gel method, are useful and promising photocatalysts to be used in liquid-phase reactions.

As described above, in situ photoluminescence, UV−vis reflectance, FT-IR, ESR, XAFS, XRD, and XPS spectroscopic investigations of these Ti/Si binary oxides indicated that the titanium oxide species are highly dispersed in the SiO_2 matrixes and exist in a tetrahedral coordination. Such titanium oxide species exhibited the distinct and characteristic photoluminescence, and its yield increased when the Ti content in the Ti/Si binary oxides was decreased. As shown in Figure 8, a parallel relationship between the specific photocatalytic reactivities of the titanium oxide species and the yields of the photoluminescence of the Ti/Si binary oxide catalysts can clearly be seen. It is clear that the high photocatalytic reactivity of the Ti/Si binary oxides is closely associated with the formation of the charge-transfer excited complexes of the highly dispersed tetrahedral titanium oxide species and their high reactivities.

On the other hand, such photocatalytic reactivity could not be observed for Ti/Si binary oxides in the middle region of Ti content of about 50 wt % TiO_2. XPS and XRD investigations of the catalysts suggested that the segregation of SiO_2 in the surface regions of the binary oxides is remarkable for the catalyst having a Ti content of about 50 wt % TiO_2. The covering of the titanium oxide species with such SiO_2 moieties suppresses and disturbs the accessibility of the reactant molecules with the active site of the titanium oxide species, resulting in a dramatic decrease in the photocatalytic reactivity of the catalysts.

Conclusions

Ti/Si binary oxides having different Ti content were prepared using the sol−gel method and used as photocatalysts. When the Ti content is decreased, the crystalline structure of the titanium oxides changes from aggregates in an anatase phase to ultrafine species in an amorphous state. In Ti/Si binary oxides having lower Ti content the isolated titanium oxide species in tetrahedral coordination were present separately from each other in the SiO_2 matrixes and exhibited a characteristic photoluminescence spectrum attributed to the radiative decay from the charge-transfer excited state of these species. The excited state of these tetrahedrally coordinated titanium oxide species plays a significant role in the liquid-phase photocatalytic oxidation of 1-octanol to 1-octanal as an active site, their roles being similar to the photocatalysis in the gas phase.

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