This could result from the competitive adsorption of thiophene and pyridine at Lewis acid sites on the surface. Brønsted surface acidity was also shown to be important by correlations of HDS activity with the concentration of sulfhydryl surface groups.[40,41]

The results presented here show that although surface defects and acidity are important in HDS, there is not a simple correlation. Oxide surfaces were found to be acidic relative to π-bonded benzene and thiophene. However, sulfided surfaces appeared to be acidic toward π-bonded thiophene but not benzene. In addition, oxide surfaces were not very effective for desulfurization, but sulfided surfaces were. The results suggest that specific interactions (such as S–S bonding) may be important in determining catalytic activity, and must be considered in any correlation.

Conclusions

The results presented here suggest that a transition-metal surface can be a reagent in redox and acid–base reactions. A clean tungsten surface was an extremely strong reductant, totally decomposing organic molecules to adsorbed atomic constituents. The reducing strength of the surface could be reduced by preoxidation with oxygen or sulfur. Highly oxidized surfaces changed in character from electron donors to electron acceptors. The oxidized

surfaces were acidic and could form acid-base adducts with π-electron donors such as benzene and thiophene. The acid strength of the surface was found to be very dependent on the base that was being adsorbed. Adsorbed sulfur appeared to facilitate thiophene adsorption on sulfided W(211), whereas benzene adsorption was inhibitited.

A comparison of the reactivity of benzene, thiophene and tetrahydrothiophene indicates that the aromatic character of thiophene is the most dominant feature in determining reactivity. Both thiophene and benzene acted as π-electron donors forming acid–base adducts with acidic surface oxides. Tetrahydrothiophene appeared to adsorb by electrophilic interactions between a lone pair of electrons on the sulfur atom and the surface. Thiophene was found to be more reactive than benzene and undergo electrophilic attack at the 2-position on the ring, facilitating desulfurization. THT seemed to undergo desulfurization by C–S bond scission to a thioxy intermediate and subsequent C–S bond scission to a C_4 hydrocarbon and adsorbed sulfur. These results are consistent with the hypothesis that HDS of thiophene occurs at anion vacancies in sulfided tungsten. These vacancies are electrophiles which promote electrophilic attack. The results also suggest that sulfides may adsorb by disulfide linkages and undergo desulfurization in the absence of anion vacancies.

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Photoluminescence and Photocatalytic Activity of Highly Dispersed Titanium Oxide Anchored onto Porous Vycor Glass

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Photoluminescence studies of titanium oxide anchored onto porous Vycor glass have been carried out in connection with its photocatalytic activity. The efficient quenching of photoluminescence with O_2 or N_2O and a considerable blue shift in the absorption spectrum suggest that the X-ray amorphous titanium–oxygen moiety of the catalyst is highly dispersed in the form of an individual complex on the surface. This suggests the formation of a charge-transfer excited complex, which is confirmed by appearance of a vibrational fine structure of the photoluminescence at 77 K. It is proposed that the photoluminescence quenching is closely associated with the electron transfer from the excited states of the catalyst to the added O_2 or N_2O molecules. Photocatalytic activity as well as photoluminescence intensity of the anchored catalyst is much higher than those of bulk TiO_2 catalyst, as a result of the high dispersion of Ti ions and/or the coordinative unsaturation of surface Ti ions.

Introduction

Since the pioneering work by the late Tench et al.,[1] the photoluminescence technique has been widely used to investigate the structure and properties of the active sites on the surface of supported[2,3] or bulk metal oxides,[4,5] zeolites,[6] etc., because of photoluminescence's high sensitivity and nondestructiveness of the surfaces. Recently, we have shown that the measurements of the lifetimes of photoluminescence together with its yields and

shape could provide detailed and useful information about characteristics of the emitting sites dispersed on the supports.[7]

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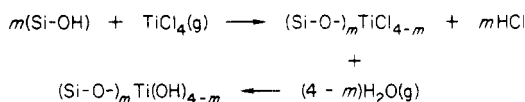
The photoluminescence techniques have been again given a great deal of attention in the field of photocatalysis over solid semiconductors as a useful probe for understanding the surface processes in which photoformed electrons and holes takes part, i.e., primary processes in photocatalysis.[2,4,7,8]

Although it is well established that surface ions in low coordination play a significant role in heterogeneous catalysis, their role is still unclear in photocatalysis.[7,9] In order to investigate this problem, chemical treatments to functionalize the surface can be used in order to control the degree of coordinative unsaturation of surface ions.[10] Recently, we have reported that with the titanium oxide anchored onto porous Vycor glass the photoformation of N_2O^- and O_2^- anion radicals as well as electron transfer from N_2O^- to the added O_2 molecules takes place even at 77 K.[9]

Lyashenko et al. have investigated the photooxidation of isobutene over the titanium oxide anchored onto silica and reported that selectivity for acetone formation is higher as compared to the case of bulk TiO_2.[11] Their work suggests the possibility of anchored titanium oxide as a useful photocatalyst, at least for the photooxidation reaction. However, the true nature of the structure and reactivity of the excited states of the anchored titanium oxides is still unknown. It is of special interest to compare the photocatalytic activity of such anchored oxide catalyst with that of usual bulk oxide catalysts or impregnated oxide catalysts. There seems to be no report along this line. Therefore, using photoluminescence techniques and photoreaction products analysis, we have investigated the excited states of the titanium oxide anchored onto porous Vycor glass and its photocatalytic activity.

Experimental Section

The anchoring (in the previous paper[9] we used "grafting" instead of "anchoring") was performed via the reaction of titanium(IV) chloride with the surface hydroxyl groups of porous Vycor glass (PVG) (Corning Code 7930-746685; BET surface area 150 m^2/g; major composition $SiO_2 > 95\%$) in the gas phase at 453–473 K, followed by treatment with water vapor to replace the chlorine atoms. According to Kol'tsov et al.[12] and Armistesd et al.,[13] these processes can be represented as follows:

$$m(\text{Si-OH}) + \text{TiCl}_4(g) \longrightarrow (\text{Si-O-})_m\text{TiCl}_{4-m} + m\text{HCl}$$

$$+$$

$$(\text{Si-O-})_m\text{Ti(OH)}_{4-m} \longleftarrow (4 - m)\text{H}_2\text{O}(g)$$

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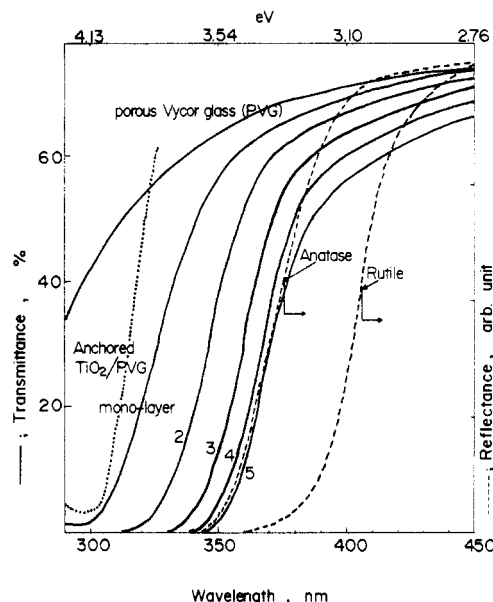

Figure 1. UV-visible absorption spectra of porous Vycor glass (PVG) and titanium oxide anchored onto PVG with 1–5 titanium–oxygen layers. The dotted line is the absorption spectrum of anchored titanium oxide with one titanium–oxygen layer obtained by subtracting the PVG spectrum from the anchored TiO_2/PVG spectrum.

It is suggested that one $TiCl_4$ reacts with two OH groups, when the silica is partially dehydrated.[10b] The number of surface OH groups on the surface of PVG was controlled by changing the degassing temperature of PVG, since the correlation between the number of remaining surface OH groups and the degassing temperatures is well established.[14] After the anchoring step, the catalysts were degassed at around 473 K, calcined in oxygen at around 873 K, and finally degassed at 453–473 K before use. The surface titanium compound formed on PVG can be dissolved in acid solution. Titanium ions can be removed completely from the surface by treatment with boiling H_2SO_4, and the titanium content was determined by colorimetric analysis. The concentration of titanium ions anchored onto the surface of PVG, degassed at 773 K and containing ca. 4.0 OH/nm^2, was determined to be ca. 3.2 $\times 10^{-5}$ mol/g. UV irradiation was carried out with a 75-W Hg lamp through water and color filters (>290 nm) at 298 K. ESR spectra were recorded with a JES-ME-1 (X-band) spectrometer at 77 and 300 K. The absorption spectra were measured with a Shimadzu UV-210 A double-beam digital spectrophotometer measuring transmission through the samples. A quartz cell with two planar windows distant from 3 mm was used. The cell with a 1-mm-thick PVG sheet was placed just before the photomultiplier in order to minimize scattering error. The photoluminescence spectra were recorded with a Shimadzu RF-501 spectrofluorophotometer with filters to eliminate scattered light at 77 and 300 K. The experimental details can be found in our previous papers.[2,4,7,15]

Results and Discussion

Photoluminescence and Excited States of Anchored Titanium Oxides. Figure 1 shows the absorption spectra of the anchored titanium oxides. The absorption spectrum of the catalyst having one TiO_2 layer is observed at shorter wavelength as compared to that of TiO_2 crystallites, its absorption maximum appearing at around 4.1 eV (ca. 300 nm). The absorption spectrum of anchored TiO_2 was obtained by subtracting PVG's spectrum from the anchored catalyst's spectrum in Figure 1. Lyashenko et al.[11] have reported that one TiO_2 layer anchored on silica exhibits an ab-

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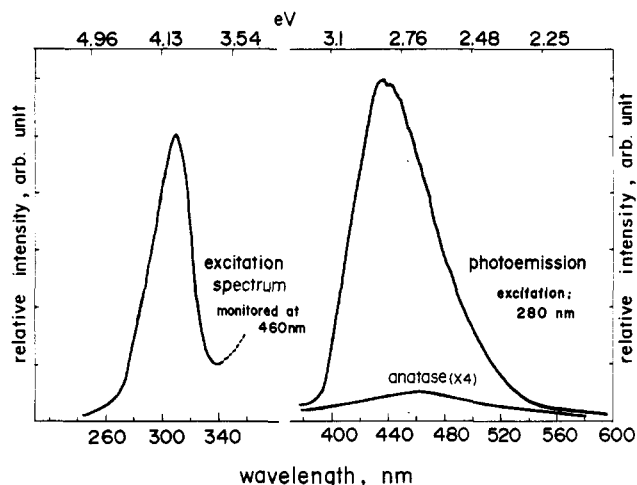(15) Anpo, M.; Yun, C.; Kubokawa, Y. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1014.

Figure 2. Photoluminescence spectrum and its excitation spectrum at 77 K of titanium oxide anchored onto porous Vycor glass (excitation wavelength 280 ± 10 nm; emission slit width 10 nm). The anchored catalyst was degassed at 423 K, and anatase TiO_2 powder was degassed at 573 K.

sorption spectrum at around 4.8 eV (ca. 260 nm) to 3.1 eV (ca. 400 nm) having a peak at 4.1 eV (ca. 300 nm) and attributed it to the charge-transfer processes involving electron transfer from the molecular orbital t_{2u}, localized on the oxygen, to the vacant t_{2g} orbital of the titanium ion. Quantum chemical calculations of the model complex suggest that this transition occurs by the absorption of ca. 3.69-eV (340-nm) light.[16] The absorption spectrum of the catalyst with one TiO_2 layer anchored (Figure 1) seems to be in good agreement with their results. Furthermore, X-ray diffraction studies show that no line due to TiO_2 can be detected for this catalyst with one TiO_2 layer. These results suggest that the catalyst with only one TiO_2 layer is characterized by the assembly of individual titanium–oxygen complexes on the PVG surface and that as a crystal phase of TiO_2 is not formed.

When the number of TiO_2 layers is increased, the absorption spectrum is shifted to longer wavelength region, approaching that of bulk TiO_2 (anatase) at four or five TiO_2 layers. According to X-ray studies by Kol'tsov et al.,[12] the anchored TiO_2 is X-ray amorphous up to three layers of TiO_2, while above this number weak diffraction lines due to anatase can be observed. Our results appear to confirm the finding of Kol'tsov et al.[12] With increasing number of TiO_2 layers, the interaction of the individual titanium–oxygen complexes becomes stronger. As a result, the energy levels of those complexes are no longer defined strictly and a band structure emerges, explaining the shift to longer wavelength.

In the following, we consider only the catalyst with one anchored TiO_2 layer. Its photoluminescence spectrum is shown in Figure 2, which also includes its excitation spectrum monitored at 460-nm emission at 77 K as well as the photoluminescence spectrum of TiO_2 powders (anatase), which were prepared by slow hydrolysis of $TiCl_4$ in dilute ammonium solution, dried, and then calcined in oxygen at 773 K. Although there is no marked difference in the position of the peaks observed with bulk (ca. 460 nm) and anchored TiO_2 (ca. 440 nm), the intensity is much higher for the latter than for the former. It is also seen that the excitation spectrum of the anchored TiO_2 is essentially the same as its absorption spectrum shown in Figure 1.

Figure 3 shows the vibrational fine structure of the photoluminescence spectrum of the anchored catalyst observed at 77 K. The energy separation between the (0 → 0) and (0 → 1) band of the vibrational transition bands, which corresponds to the energy obtained by the IR spectrum, belongs to the region of the vibration of the Ti–O bond (i.e., 720–820 cm^{-1}),[17] and the agreement is particularly good with an absorption maximum at ca. 780 cm^{-1}

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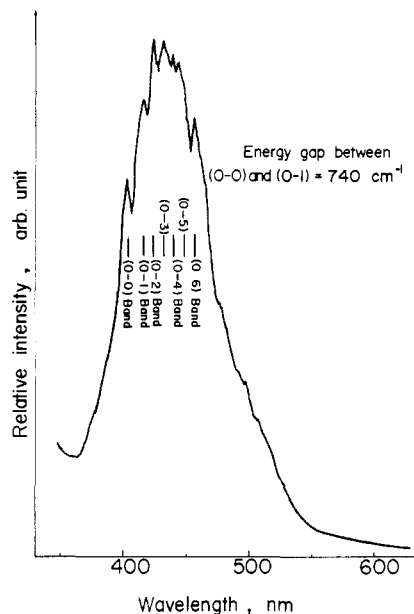

Figure 3. Fine structure of photoluminescence at 77 K of the titanium oxide anchored onto porous Vycor glass (excitation wavelength 280 ± 10 nm; emission slit width 2.6 nm).
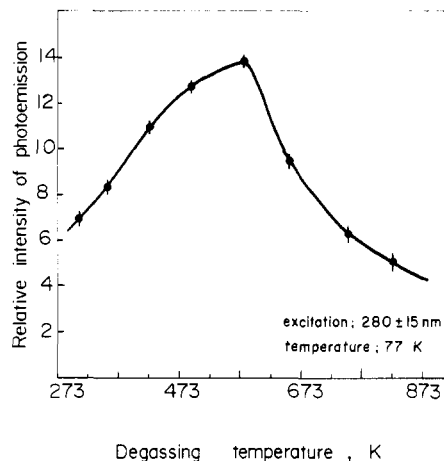

Figure 4. Effect of the degassing temperature of catalyst upon the yield of photoluminescence of the anchored titanium oxide catalyst at 77 K (excitation wavelength 280 ± 15 nm). Catalysts were degassed for ca. 15 min at each temperature.

obtained for the titanium oxide anchored onto silica.[12] As described above, the absorption of light corresponding to the charge-transfer bands brings about electron transfer from oxygen to titanium ion, i.e., resulting in the formation of a pair of hole center (O^-) and trapped electron center (Ti^{3+}). The appearance of such vibrational fine structure suggests that the photon energy absorbed by the catalyst is mainly localized on the titanium–oxygen bonds. Recently, we have reported that the vibrational fine structure of the phosphorescence of V_2O_5 supported on PVG shows the strongest peak at the (0 → 3) transition,[2] while that of powdered ZnO is at the (0 → 1) transition.[4] The Franck–Condon principle suggests that the internuclear distance in the V=O complex becomes longer in the charge-transfer excited states, while for ZnO, its does not change very much. Such features are in agreement with what is expected from the results of the photoreduction of these oxides with CO molecules.[2,4] As shown in Figure 3, the (0 → 3) transition is the strongest in the case of anchored catalysts, suggesting that the internuclear Ti–O distance will increase in the excited state as compared to that in the ground state.

The effect of degassing temperature of anchored TiO_2 upon the photoluminescence intensity has been investigated in the range of temperature 300–823 K. As shown in Figure 4, with increasing
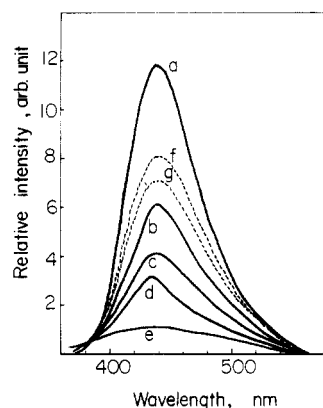
Figure 5. Effect of the addition of O_2 or N_2O upon the photoluminescence of the anchored titanium oxide catalyst at 300 K (the catalyst was degassed at 423 K, and then O_2 or N_2O molecules were introduced onto the catalyst at 300 K; excitation wavelength 280 ± 10 nm; emission slit width 7.5 nm): a, after degassing at 423 K; b, O_2 (1.2 torr); c, O_2 (6.0 torr); d, O_2 (20 torr); e, O_2 (ca. 100 torr); f, N_2O (3.0 torr); g, N_2O (5.1 torr).
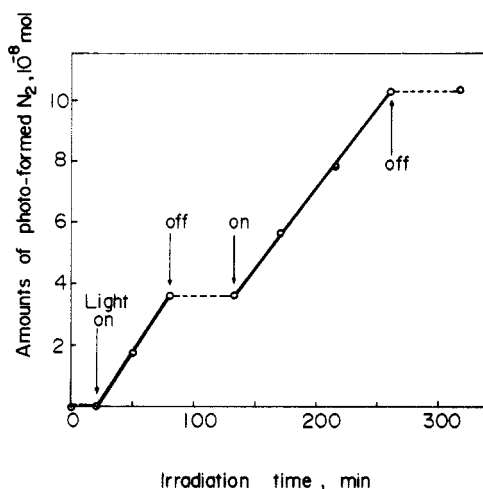

Figure 6. Photoformation of N_2 molecules from N_2O molecules over the anchored titanium oxide catalyst at 300 K (UV excitation wavelength, >290 nm; amount of the catalyst used, 0.9 g; initial pressure of N_2O, 1.1 torr).

degassing temperature the intensity of photoluminescence increases up to 573 K, showing a maximum, and then decreases. Such behavior can be explained as follows: Owing to desorption of adsorbed species such as oxygen and water, the intensity of the photoluminescence will increase up to the degassing temperature of about 573 K. Above this temperature, the intensity will decrease because of the decomposition of the titanium–oxygen complexes, since according to the work by Kol'tsov et al. this complex is stable up to 623 K.[12] Degassing above 573 K would cause the destruction of the emitting sites to start.

Quenching and Reactivity of Excited States of the Anchored Titanium Oxide. As shown in Figure 5, the addition of O_2 molecules at 77 or 300 K onto the anchored catalyst leads to efficient quenching of the photoluminescence at 77 or 300 K. The intensity recovery was observed with evacuation of the catalyst at 300 K, though it was not complete (ca. 90–95%). The effect of the addition of N_2O on the intensity of the photoluminescence was also investigated, because of its high efficiency for electron trapping. On introduction of N_2O onto the catalyst, the photoluminescence decreases in intensity with an efficiency lower than that of O_2 (Figure 5). Such an efficient quenching of photoluminescence with O_2 or N_2O molecules will be expected when emitting sites are dispersed on the surface, because of efficient interaction with quenchers. As shown in Figure 6, on UV irradiation of the catalyst in the presence of N_2O, the evolution of N_2 molecules takes place immediately, its yield increasing with
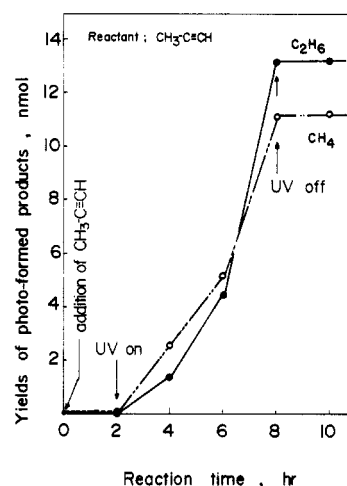

Figure 7. Photohydrogenation of CH_3—C≡CH with H_2O over the titanium oxide anchored onto PVG (UV excitation wavelength, >290 nm; reaction temperature, 300 K; amount of catalyst used, 0.4 g; initial pressure of CH_3—C≡CH, 3.0 torr; initial pressure of H_2O, 5.0 torr). C_3H_6 was produced as a minor product.

irradiation time. As soon as the UV irradiation ceases, the reaction stops immediately. Such evolution of N_2 molecules suggests that the photocatalytic decomposition of N_2O proceeds under UV irradiation at 300 K. Blyholder et al.[18] and Lunsford et al.[19] have reported that photocatalytic decomposition of N_2O proceeds via N_2O^- intermediates over ZnO. Cunningham et al. have also reported that the decomposition of N_2O is photoinduced over ZnO through the trapping of photoformed electrons by N_2O molecules,[20] though with TiO_2 powders degassed at 683 K the absence of photodecomposition has been reported.[21]

In connection with this problem, ESR measurements were undertaken under UV irradiation at 77 K. UV irradiation of the catalyst in the presence of N_2O was found to give a new triplet ESR signal at $g = 2.0029$ assigned to N_2O^- anion radicals, as described in a previous paper.[9] With O_2 molecules, UV irradiation mainly led to the formation of O_2^- anion radicals. Apart from the appearance of these species, which will be discussed in the following paper, the ESR results suggest that the decrease in the photoluminescence by the addition of O_2 or N_2O molecules is closely associated with the quenching of the excited states of the anchored titanium oxide, which includes electron-transfer processes from the excited catalyst to the added molecules. This concept would be well supported by the facts that O_2 molecules quench the photoluminescence more efficiently than N_2O molecules as shown in Figure 5, the former having a larger electron affinity than that of the latter.

High Efficiency of Anchored Titanium Oxide Photocatalysts. As described previously,[22] the photocatalytic reactions of water with various unsaturated hydrocarbons such as alkynes or alkenes over TiO_2 powders have provided useful information on the nature of photocatalysis. We have now extended these studies to anchored titanium oxide catalysts. As shown in Figure 7, UV irradiation of the anchored catalyst in the presence of H_2O and CH_3—C≡CH at 300 K leads to the formation of CH_4 and C_2H_6; their yields increase with UV irradiation time, and when UV irradiation is ceased their formation stops immediately. C_3H_6 was also photoformed as a minor product. As described in our previous papers, two types of photoreactions can occur: photohydrogenation with or without fission of the triple bond of CH_3—C≡CH, CH_4 and C_2H_6 arising from the former and C_3H_6 from the latter. It has been suggested that the C≡C bond fission accompanied by the photohydrogenation reaction, i.e., photohydrogenolysis, is closely

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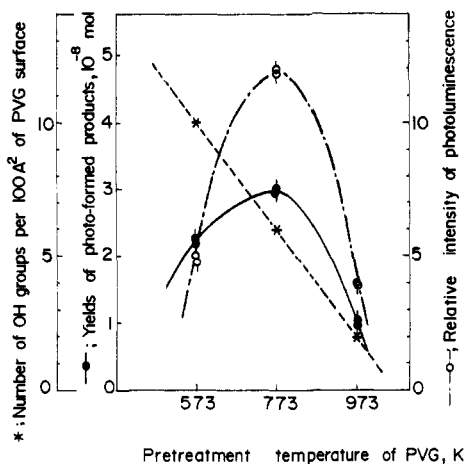
Figure 8. Effect of the pretreatment temperature of PVG upon the yields of photohydrogenation reaction of CH_3—$C\equiv CH$ with H_2O and of photoluminescence of the anchored titanium oxide catalyst at 300 K (UV excitation wavelength >290 nm; reaction temperature, 300 K; initial pressure of CH_3—$C\equiv CH$, 3.0 torr; initial pressure of H_2O 5.0 torr; excitation wavelength for photoluminescence, 280 ± 10 nm; emission slit width, 7.0 nm).

TABLE I: Photohydrogenation Reactions of CH_3—$C\equiv CH$ with H_2O over Anchored Titanium Oxide Catalyst at 300 K[a]

pressure of H_2O, torr	yields of photohydrogenation products, 10^{-9} mol/h			selectivity = $(CH_4 + C_2H_6)/C_3H_6$
	CH_4	C_2H_6	C_3H_6	
0	25.1	10.3	1.5	23.6
3.0	55.0	100.3	2.1	73.8

[a] Pressure of CH_3—$C\equiv CH$, 3.0 torr; amount of catalyst used, 0.4 g; content of anchored TiO_2, 0.25 wt %; excitation wavelength, >290 nm.

associated with the coexistence of photoformed electron and hole, i.e., Ti^{3+} and $\dot{O}H$ (or O^-), while photohydrogenation without bond fission proceeds via a photoelectrochemical mechanism which requires complete separation of electron and hole. Accordingly, such high selectivity for photohydrogenation with $C\equiv C$ bond fission is expected over the anchored catalyst, since the separation of photoformed electron and hole appears to be difficult over highly dispersed titanium oxide.

As described above, the amount of titanium ions fixed onto the surface of PVG is easily controlled by changing the concentration of surface OH groups, i.e., by changing the pretreatment temperature of PVG before the anchoring reaction. Figure 8 shows that the yields of photocatalytic reactions of CH_3—$C\equiv CH$ with

H_2O change in a manner similar to the intensity of photoluminescence. Since the photoluminescence originates from the presence of the excited complex, $[Ti^{3+}-O^-]^*$ described above, this complex plays a significant role in the photocatalytic reactions of water with CH_3—$C\equiv CH$ over the anchored TiO_2 catalyst. Details of the photocatalytic reactions will be reported in the near future.

The initial rate of photocatalytic hydrogenation accompanying the triple-bond fission of CH_3—$C\equiv CH$ over the anchored catalyst is determined to be about 88 nmol/(h g of cat.), while with bulk rutile TiO_2 powders that value is about 13 nmol/(h g of cat.) (apparent quantum yield is less than 0.0005 with rutile),[22] as shown in Table I. However, it must be stressed here that the concentration of operating titanium ions for the anchored catalyst is only about 3.2×10^{-5} mol/g of cat., while that for bulk TiO_2 is 1.25×10^{-2} mol/g of cat. As a result, it is concluded that the photocatalytic activity of the anchored titanium oxide is much higher than that of bulk TiO_2 by about 2 or 3 orders of magnitude. Such high photocatalytic activity of the anchored catalysts would arise from the presence of highly dispersed TiO_2 and/or its coordination unsaturation, which results in less efficient radiationless transfer of photon energy absorbed by the catalysts. Recently, with MoO_3 highly dispersed on PVG it has been concluded that similar less efficient radiationless transfer of photon energy results in high yields for photocatalytic reactions as well as photoluminescence, the significance of tetrahedral coordination of highly dispersed Mo ions being pointed out.[7,23] In relation to this concept, it is worth mentioning that photocatalytic activity of TiO_2 in the binary Ti–Si oxides catalysts is enhanced in the region of low TiO_2 content where Ti ions are present separately from each other in the SiO_2 carrier matrix.[24] Furthermore, Gesser et al. have reported that porous titania glass, having SiO_2 as the major component, exhibits a high photocatalytic activity.[25] Although the true nature of such enhancement of photocatalytic activity is not clear at the present, a similar explanation to that described above would be applicable. To settle these problems, various anchored oxide catalysts are being investigated in our laboratory. Thus, the present work not only provides useful information on the nature and properties of the anchored oxide catalysts but also shows the high efficiency of highly dispersed TiO_2 photocatalysts.

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