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Photocatalysis over Binary Metal Oxides. Enhancement of the Photocatalytic Activity of TiO_2 in Titanium–Silicon Oxides

Masakazu Anpo,* Hiroaki Nakaya, Sukeya Kodama, Yutaka Kubokawa,

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 591, Japan

Kazunari Domen, and Takaharu Onishi

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259-Nagatsuta, Midori-ku, Yokohama 227, Japan *(Received: August 28, 1985)*

Photocatalytic reactions of alkenes and alkynes with water were investigated over titanium–silicon oxides in order to obtain information about the potential ability of binary oxides as photocatalysts. Photocatalytic activity of TiO_2 species in the titanium–silicon oxides was found to be enhanced in the region of lower Ti content. X-ray, photoluminescence, and X-ray photoelectron spectroscopy (XPS) measurements indicate that Ti ions are enriched on the surface of the oxides having a low Ti content and present separately from each other in the SiO_2 matrix. From these results, together with those obtained with highly dispersed TiO_2 anchored on support surfaces, it is suggested that the higher photocatalytic activity of such catalysts is due to the diminished radiationless transfer of the photon energy absorbed by TiO_2.

Introduction

Since the pioneering works by Honda and Fujishima[1] and Schrauzer and Guth,[2] photocatalysis with various semiconductors has been investigated by a number of workers.[3] Most of them were devoted to design of the photocatalyst system with high conversion of light into chemical energy. Recent studies were focused on colloidal semiconductors,[4] on extremely small sized particles in which quantization effects are expected,[5] as well as with semiconductors on inert supports.[6] Various binary oxide catalysts seem to be potentially promising, since it is well-known that binary oxide catalysts often exhibit higher catalytic activity and selectivity than what one can predict from the properties of their components. However, few studies have been carried out on photocatalysis over binary oxide catalysts. Domen et al.[7] reported that the photocatalytic activity of $SrTiO_3$ for the decomposition of water is enhanced by the addition of NiO. Recently, Bard et al.[8] showed that in the same reaction the photocatalytic activity of $ZnS{\cdot}CdS/SiO_2$ is higher than those of its components. These results suggest that binary metal oxides are potentially useful photocatalysts. In the present work, we report on the photocatalytic reactions of H_2O with unsaturated hydrocarbons such as $CH_3{-}C{\equiv}CH$ or $CH_3{-}CH{=}CH_2$ over titanium–silicon oxide catalysts. The characteristics of these reactions were clarified by previous workers.[2,9] We report the enhancement of the photocatalytic activity of the TiO_2 species in the titanium–silicon oxides having a lower Ti content. Recently, we have reported that highly dispersed TiO_2 catalysts anchored onto porous Vycor glass exhibit much higher photocatalytic activity for the photohydrogenation reaction of $CH_3{-}C{\equiv}CH$ with H_2O as compared to that of the usual bulk TiO_2 powders due to the high dispersion of Ti ions and/or the coordinative unsaturation of surface Ti ions.[10] It is of special interest, therefore, to compare the structure and reactivity of TiO_2 species in the titanium–silicon oxide catalysts having lower Ti content than with that of the anchored TiO_2 catalysts.

Experimental Section

Catalysts. Titanium–silicon oxide catalysts having different molar percent of Ti were prepared by coprecipitation of desired amounts of mixed solution of $(C_2H_5O)_4Si$ and $TiCl_4$ by addition of dilute aqueous solution of ammonia.[11] The washed and dried material was converted to binary metal oxide by the thermal decomposition at 773 K in air. The binary oxide catalysts were degassed under vacuum at 777 K, heated in oxygen at the same temperature, and finally degassed before use as photocatalysts.

Apparatus and Procedure. X-ray diffraction patterns of the catalysts were obtained on a Rigaku RDA-rA X-ray diffractometer using Cu Kα radiation with a Ni filter. Photoluminescence was measured at 77 and 298 K by using a Shimadzu RF-501 spectrofluorophotometer. Absorption spectra were measured by a Shimadzu UV-210 A double-beam digital spectrophotometer equipped with conventional components of a reflectance spectrometer at 298 K. XPS was measured at 298 K by using a Shimadzu ESCA-750 photoelectron spectrometer. The degassed samples were mounted on double-sided adhesive tape in an Ar-filled glovebox. Binding energies were corrected for samples charging by reference to Au evaporated onto the sample by vacuum deposition.

UV irradiation was carried out with a 75-W Hg lamp ($\lambda > 300$ nm) at 298 K. The catalysts were spread on the quartz window, having a surface area of about 30 cm^2, of the cell, having a total

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TABLE I: Results of the Photocatalytic Reactions of $CH_3—CH=CH_2$ with H_2O over the Binary Titanium–Silicon Oxide Catalysts at 298 K[a]

composn, %	yields of photohydrogenation products, 10^{-6} mol/h				specific photocatalytic
TiO_2:SiO_2	CH_4	C_2H_6	C_3H_8	total	activity of TiO_2
100:0	0.250	2.78	0.010	3.124	1.00
90:10	0.084	0.620	0.280	1.004	0.36
50:50	0.040	0.160	0.071	0.273	0.17
20:80	0.058	0.222	0.101	0.382	0.61
14:86	0.090	0.341	0.138	0.569	1.30
10:90	0.116	0.466	0.143	0.724	2.32
8:92	0.150	0.650	0.240	1.540	6.12
9:97	0.142	0.632	0.204	1.054	11.3
0:100	0	0	0	0.0	0.0

[a] The amount of catalyst used was 0.5 g. H_2O vapor was adsorbed at 298 K until a pressure of 1.3 kPa was reached, after which the evacuation was carried out at the same temperature. The pressure of $CH_3—CH=CH_2$ was 4.0 kPa. Other minor products were C_2H_4, C_4H_{10}, and C_4H_8.

TABLE II: Results of the Photocatalytic Reactions of $CH_3—C\equiv CH$ with H_2O over the Binary Titanium–Silicon Oxide Catalysts at 298 K[a]

composn, %	yields of photohydrogenation products, 10^{-6} mol/h				specific photocatalytic
TiO:SiO_2	CH_4	C_2H_6	C_3H_6	total	activity of TiO_2
100:0	1.470	18.60	1.308	25.32	1.00
90:10	0.243	3.210	1.810	6.533	0.28
50:50	0.065	0.513	0.780	1.422	0.10
10:90	0.082	6.510	0.920	7.520	2.31
8:92	0.104	7.970	0.780	9.810	3.74
3:97	0.058	4.330	0.320	4.731	5.60
0:100	0	0	0	0.0	0.0

[a] The amount of catalyst used was 0.5 kg. The pressure of $CH_3—C\equiv CH$ was 4.0 kPa. H_2O vapor was adsorbed at 298 K until a pressure of 1.3 kPa was reached, after which the evacuation was carried out at the same temperature.

volume of about 50 cm^3. H_2O vapor was adsorbed onto the catalyst at 298 K until a pressure of 1.3 kPa (10 torr) was reached, after which the evacuation was carried out at the same temperature. As described previously,[9] after this treatment adsorbed water remains on the surface in two forms, i.e., molecular water and surface hydroxyl groups. Then, the reactant was introduced onto the catalyst at a pressure of 4.0 kPa (30 torr) at 298 K. Detailed procedures have been described in our previous papers.[9,12]

The BET surface area of the catalysts determined by N_2 adsorption increased with increasing Si content (TiO_2 alone; 80 m^2/g), passing through a maximum at about 50% of TiO_2 (titanium–silicon oxide with 50% of TiO_2; 300 m^2/g), and then decreased with increasing Si content (SiO_2 alone; about 250 m^2/g). It was found that there is no correlation between the photocatalytic activity of the binary oxide catalysts and the their surface area. Such features are expected, since the photocatalytic reaction proceeds over only the surface exposed to UV irradiation.

Results and Discussion

Tables I and II show the yields of the hydrogenation products in the photocatalytic reactions of H_2O with $CH_3—CH=CH_2$ and $CH_3—C\equiv CH$ over the titanium–silicon oxide catalysts. As shown in a previous paper,[9] the products accompanied by the C=C bond (for alkenes) or C≡C bond (for alkynes) fission such as CH_4 and C_2H_6 constitute the major products. As described previously,[9] such features are in good agreement with those observed with metal-free TiO_2 catalysts, being attributable to the close existence of photoformed electron and hole, i.e., Ti^{3+}–O^- (or Ti^{3+}–$\dot{O}H$) pair species. Such trapped electron and hole pairs will interact with the alkyne (or alkene) adsorbed on the surface to form the carbenes and oxygen-containing compounds in a manner similar to that described previously,[9,13] while with Pt-loaded TiO_2, where the photoelectrochemical mechanism is operating, the hydrogenation products without the C=C or C≡C bond fission are predominant.[12] With Pt-loaded (4 wt %) titanium–silicon oxide catalysts formation of C_3H_6 (from $CH_3—C\equiv CH$) and C_3H_8 (from $CH_3—CH=CH_2$) was found to be the major photohydrogenation products, being in agreement with those obtained with Pt-loaded TiO_2 catalysts.[12] As shown in Tables I and II, the yields of photohydrogenation products drastically decrease first with increasing Si content; however, an increase in the yields is observed in the region of low Ti contents. Tables I and II also show the specific photocatalytic activity of TiO_2 species, i.e., (yields of photoformed products)/(TiO_2 content) of the titanium–silicon oxide catalysts. The specific photocatalytic activity of TiO_2 increases remarkedly in the region of the lower Ti content. A similar feature is observed with mixtures of TiO_2 and SiO_2, its extent being much smaller than that of the titanium–silicon oxide catalysts (Figure 1). On the other hand, as shown in Figure 1, with titanium–zinc oxide catalysts the yields of photohydrogenation reactions exhibit no increase, decreasing monotonously to a negligible value with decreasing Ti content. It is well-known that trapping or recombination centers are formed by addition of a foreign material to a semiconductor.[14] This would be the case for the titanium–zinc oxide and the titanium–silicon oxide in the

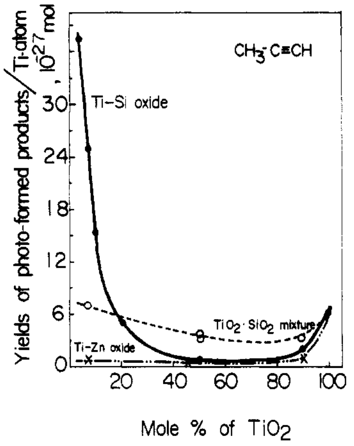

Figure 1. Changes in specific photocatalytic activity of titanium–silicon oxide catalysts, mixtures of TiO_2 and SiO_2, and titanium–zinc oxide catalysts with decreasing Ti content in catalysts. H_2O vapor was adsorbed at 298 K until a pressure of 1.3 kPa was reached, after which the degassing of the catalyst was carried out at the same temperature for 30 min (pressure of $CH_3—C\equiv CH$, 4.0 kPa).

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TABLE III: Binding Energies of Ti($2p^{3/2}$), Si($2p^{1/2}$), and Si(2s) and Ratio of the Signal Intensity of Ti($2p^{3/2}$) vs. Si($2p^{1/2}$) in the Binary Titanium–Silicon Oxide Catalysts

bulk composn of catalysts		surface characteristics of catalysts			
			binding energy,[a] eV		
TiO_2:SiO_2	TiO_2/SiO_2	Ti($2p^{3/2}$)/Si($2p^{1/2}$)	Ti($2p^{3/2}$)	Si($2p^{1/2}$)	Si(2s)
100:0	100% of TiO_2	100% of TiO_2	458.7_6		
90:10	9.00	5.85 (−35%)[b]	458.6_8	101.8_4	153.0_8
50:50	1.00	1.03 (+3.0%)	459.3_2	102.4_8	153.4_0
10:90	0.111	0.15 (+32%)	460.2_8	102.9_6	154.0_4
3:97	0.031	0.046 (+48%)	460.5_4	103.0_2	154.0_6
0:100	0	100% of SiO_2		102.9_2	154.0_8

[a] The binding energies of the Ti($2p^{3/2}$), Si($2p^{1/2}$), and Si(2s) lines were referenced to the Au($4f^{7/2}$) line (83.8 eV). The Au reference was introduced onto the sample surface by vacuum deposition. [b] Parentheses indicate the magnitude of the difference from the bulk composition. + stands for the enrichment of Ti ions in the surface region.

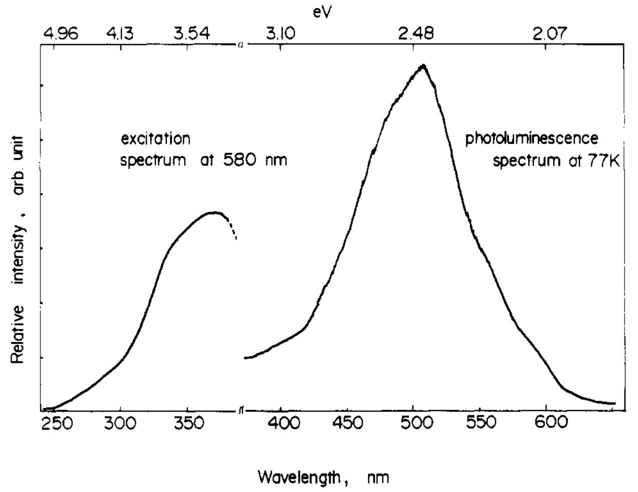

Figure 2. Photoluminescence and its excitation spectrum of titanium–silicon oxide catalysts at 77 K (Ti:Si = 1:1 composition; excitation wavelength, 300 ± 10 nm; slit width for emission, ±7.0 nm).

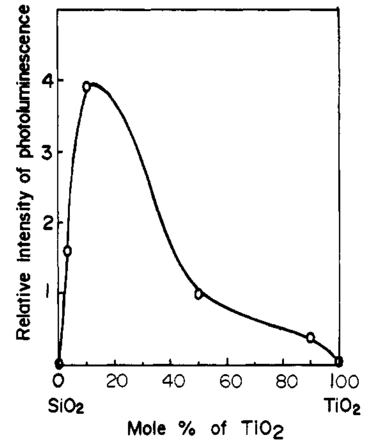

Figure 3. Changes of photoluminescence spectrum of titanium–silicon oxide catalysts in intensity with decreasing Ti content in catalysts (excitation wavelength, 300 ± 15 nm; slit width for emission, ±7.0 nm; temperature, 77 K).

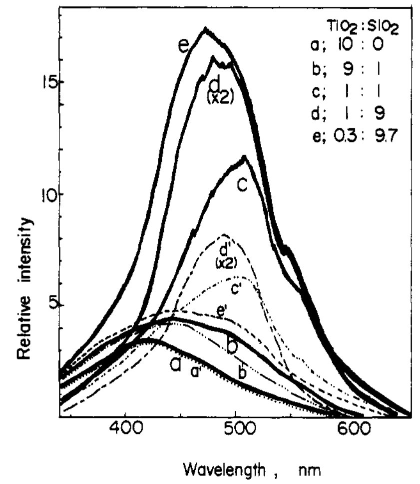

Figure 4. Photoluminescence spectra of titanium–silicon oxide catalysts at 77 K and the effect of the addition of oxygen upon them (excitation wavelength, 300 ± 15 nm; slit width for emission, ±7.0 nm; pressure of added oxygen, 1.3 kPa for a′–e′; a–e are photoluminescence in the absence of oxygen).

region of high Ti content. Although the details of the titanium–zinc oxide catalysts will be reported in a following paper, these results clearly confirm the enhancement of the photocatalytic activity of TiO_2 in the SiO_2 matrix in the region of lower Ti content.

In order to understand the nature of such an enhancement in the photocatalytic activity of TiO_2 species in the titanium–silicon oxide catalysts containing a small amount of TiO_2, the photoluminescence and XPS of the catalysts have been measured, since both techniques are very useful for the characterization of the catalyst surfaces. Figure 2 shows the photoluminescence and its excitation spectrum of the titanium–silicon oxide catalyst (Ti:Si = 1:1). Pure TiO_2 powders exhibit a weak photoluminescence at around 440 nm, being in agreement with previous data.[10,15] With the titnaium–silicon oxide catalysts a new photoluminescence appears at around 500 nm, its peak and λ_{max} of its excitation spectrum shifting steadly toward shorter wavelength with decreasing Ti content. This behavior seems to be coincident with the blue shift in the reflectance spectra of these catalysts (vide infra). The addition of oxygen onto the catalysts leads to the efficient quenching of the photoluminescence, indicating that the photoluminescence is a surface phenomenon and not associated with the bulk. Figure 3 shows the change in intensity of photoluminescence with decreasing Ti content. It is clear that the intensity of the new photoluminescence spectrum increases with decreasing Ti content, passing through a maximum, and then decreases with decreasing Ti content. Such features seem to parallel the yields of photocatalytic hydrogenation on titanium–silicon oxide catalysts (Tables I and II). Although with pure TiO_2 the addition of oxygen brings about no efficient quenching of photoluminescence, with titanium–silicon oxide ctalysts quenching occurs easily. As shown in Figure 4, there is a steady increase of the extent of the quenching with oxygen as the Si content of the titanium–silicon oxides increases. These results suggest the appearance of new emitting sites present in the surface region of the catalysts, and its lifetime becomes longer with the catalysts having lower Ti contents. It is worth mentioning that the highly dispersed TiO_2 anchored onto porous Vycor glass exhibits the photoluminescence at around 450 nm, being quenched efficiently by the added oxygen molecules.[10]

As shown in Figure 5, the X-ray patterns of the titanium–silicon oxide catalyst show only the diffraction lines due to anatase type TiO_2. With decreasing Ti content, the diffraction lines decrease in intensity, being broadened and finally disappeared, in agreement

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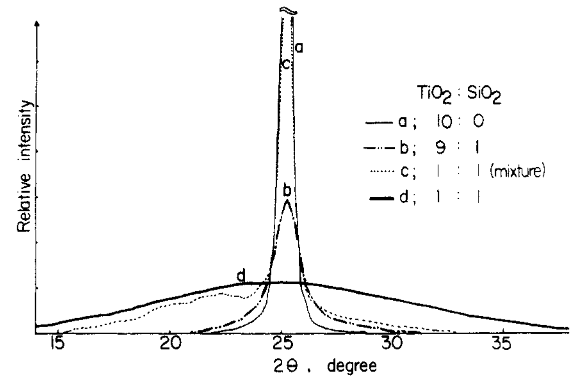

Figure 5. X-ray diffraction spectra of titanium–silicon oxide catalysts and mixture of TiO_2 and SiO_2.

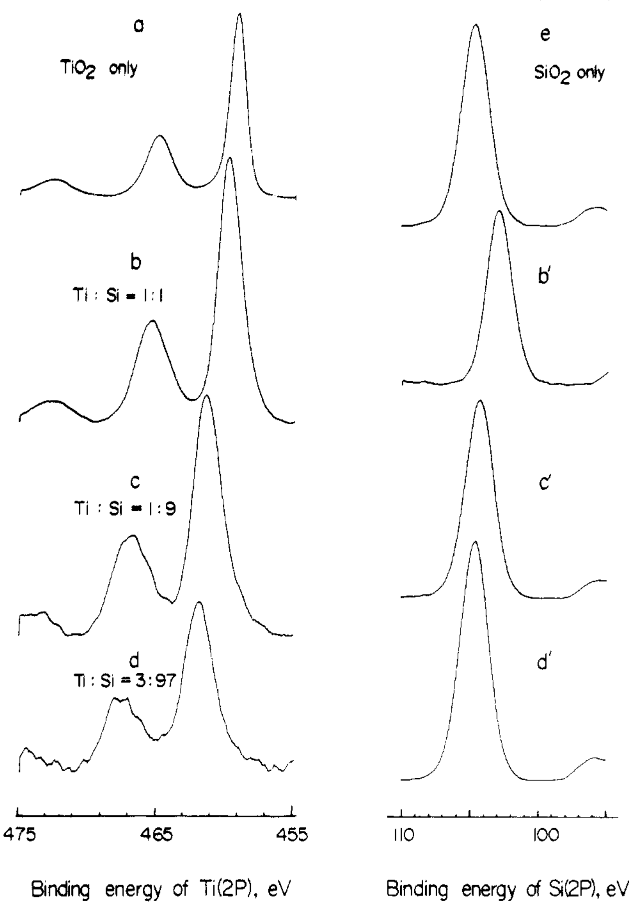

Figure 6. XPS signals for titanium–silicon oxide catalysts at 298 K.

with the results of previous workers.[11] Such features indicate that with titanium–silicon oxide catalysts the crystallinity of TiO_2 decreases drastically and disappears in the low Ti content region.

Figure 6 shows the $Ti(2p^{3/2})$ and $Si(2p^{1/2})$ XPS signals for the titanium–silicon oxide catalysts. Table III shows these XPS results. It is seen that the binding energy of the $Ti(2p^{3/2})$ band shifts to a higher value by about 1 eV with the catalysts having less then 10% Ti content. The same tendency is observed for $Si(2p^{1/2})$ or Si(2s), and their binding energies shift to higher values with increasing Si content, which may well be accounted for as originating from the pure SiO_2 as support. Table III also shows the ratio of the $Ti(2p^{3/2})$ to $Si(2p^{1/2})$ band intensity. It is clear that there is a steady increase in the intensity of $Ti(2p^{3/2})$ signals as the Si content of the titanium–silicon oxides increases. Furthermore, the ratio of the$Ti(2p^{3/2})$ to $Si(2p^{1/2})$ band intensity is higher than what is expected from the bulk composition, especially in the lower content region of Ti ion, suggesting the enrichment of Ti ions in the surface region of the catalysts having a lower Ti content. The shift in the binding energies of the $Ti(2p^{3/2})$ to higher values might arise from a smaller relaxation energy for highly dispersed TiO_2 species as compared with the case of bulk TiO_2.[16]

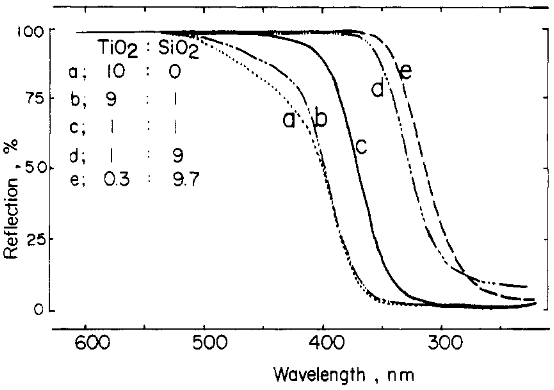

Figure 7. UV diffuse reflectance spectra of titanium–silicon oxide catalysts at 298 K (MgO powders were used for the reference).

Figure 7 shows the reflectance spectra of the titanium–silicon oxide catalysts. It is clear that with increasing Si content the absorption band of the catalysts remarkably shifts toward a shorter wavelength. Similar studies on the mixture of TiO_2 and SiO_2 having various compositions of Ti:Si were carried out for comparison. The blue shift was observed with a mixture of low TiO_2 content, its extent being smaller than those of the titanium–silicon oxide catalysts. As it has been shown previously, a considerable blue shift is observed with the absorption band of the highly dispersed TiO_2 anchored onto porous Vycor glass.[10]

All these results described above clearly indicate that with titanium–silicon oxide catalysts having a lower Ti content Ti ions are enriched in the surface region, being present separately from each other in the SiO_2 carrier matrix. At present it is unclear that the Ti ions in the surface region are present as such or as a new compound formed with SiO_2. Recently, it has been suggested that radiationless transfer of the photon energy absorbed by the oxide strongly depends on the configuration of the surface ions which constitute the oxide; i.e., less efficient radiationless energy transfer takes place on the oxide having unsaturated surface ions.[17,18] In fact, we have reported that the highly dispersed titanium oxide anchored onto porous Vycor glass exhibits much higher photocatalytic activity for the photohydrogenation reactions of $CH_3—C{\equiv}CH$ with H_2O as compared to those with usual bulk TiO_2 powders by about 2 or 3 orders of magnitude, and such high activity results from the coordinative unsaturation of Ti ions due to their high dispersion.[10] Thus, a high photocatalytic activity of TiO_2 species in the lower Ti content region of the chemically mixed binary titanium–silicon oxide catalysts is explicable in a similar manner.

Such a conclusion concerning the photocatalytic activity of the binary oxide catalysts seems to be very useful for the design of efficient photocatalytic systems. Finally, it should be noted that such an enhancement of the photocatalytic activity of highly dispersed TiO_2 would be unexpected when the reaction proceeds via the photoelectrochemical mechanism where separation of photoformed electrons and holes is important.[9,12]

Registry No. $CH_3CH{=}CH_2$, 115-07-1; $CH_3C{\equiv}CH$, 74-99-7; TiO_2, 13463-67-7; SiO_2, 7631-86-9.

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