

Photooxidation of propylene with oxygen over $\text{TiO}_2\text{-SiO}_2$ composite oxides prepared by rapid hydrolysis

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Abstract

$\text{TiO}_2\text{-SiO}_2$ composite oxides were prepared by rapid hydrolysis of a mixture of $\text{Ti}(\text{OPr}^i)_4$ and $\text{Si}(\text{OEt})_4$ in ethanol with aqueous acetic acid. Photooxidation of propylene with O_2 was carried out over $\text{TiO}_2\text{-SiO}_2$ catalysts containing 5 and 75 mol% TiO_2 , and titanasilicate (TS-1). Propylene oxide was produced only over 5 mol% $\text{TiO}_2\text{-SiO}_2$ and TS-1, where Ti species are in a tetrahedral configuration. It was postulated that propylene oxide was formed by reductive elimination via C–O bond formation in a titanaoxacyclobutane produced from photoactivated Ti–O and propylene © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Titania-silica; Photooxidation; Oxygen radical; Epoxidation; ESR; Propylene oxide; TS-1

1. Introduction

We have reported that there are two types of titanium sites in $\text{TiO}_2\text{-SiO}_2$ composite oxides prepared by rapid hydrolysis [1–3]. One is a tetrahedral site and the other is octahedral. The structure of TiO_2 reflects selective epoxidation of olefins with *t*-butyl hydroperoxide as an oxidant [1]. Oxidation with molecular oxygen is preferable from a viewpoint of economical and green chemistry.

Ohno et al. reported that liquid–solid phase photoepoxidation of hexenes with molecular oxygen proceeded in the presence of TiO_2 with considerable

selectivity [4]. They found that any TiO_2 powders were useful and P-25 TiO_2 from Japan, Aerosil was the most effective. We have tried gas–solid phase photoepoxidation of propylene with $\text{TiO}_2\text{-SiO}_2$ composite oxides prepared by rapid hydrolysis. Contrary to the liquid–solid phase photooxidation by TiO_2 [4], product distribution is dependent upon Ti content in $\text{TiO}_2\text{-SiO}_2$. We have studied the relationship between photoepoxidation of propylene and the structure of the Ti site in $\text{TiO}_2\text{-SiO}_2$.

2. Experimental

2.1. Preparation of $\text{TiO}_2\text{-SiO}_2$ composite oxides and titanasilicate

Eight kinds of $\text{TiO}_2\text{-SiO}_2$ composite oxides (Ti/Si (mol ratio) = 5/95–100/0) were prepared by

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hydrolysis of a mixture of $\text{Ti}(\text{OPr}^i)_4$ and $\text{Si}(\text{OEt})_4$ in ethanol with 0.01 M aqueous acetic acid followed by calcination at 823 K for 3 h according to the method given in the literature [5].

Titanosilicate (TS-1) was prepared from $\text{Ti}(\text{OPr}^i)_4$ and $\text{Si}(\text{OEt})_4$ according to the procedure of Notari [6,7]. The Ti content is 2.0 mol%. It was identified as TS-1 from its X-ray diffraction spectrum in comparison with the literature [6,7].

2.2. UV–VIS diffuse reflection spectroscopy

UV–VIS absorption spectra of TiO_2 – SiO_2 composite oxides without any treatment were obtained by using a Shimadzu UV-3100 spectrometer equipped with a diffuse reflection attachment. The absorption intensity was calculated from the Kubelka–Munk equation as $f(R) = (1 - R)^2/2R$, where $f(R)$ is Kubelka–Munk function and R diffuse reflection from a semi-infinite layer. The $f(R)$ is proportional to the absorption coefficient [8].

2.3. Photooxidation of propylene over TiO_2 – SiO_2 and TS-1

Photooxidation was carried out in a closed system (ca. 960 cm³) equipped with a circulation pump. The TiO_2 – SiO_2 (0.2 g) was placed in a quartz vessel (40 mm of outer diameter) and heated at 473 K in vacuo for 1 h prior to the photooxidation. Propylene (0.65 kPa) and oxygen (1.9 kPa) were admitted and irradiation was continued using a high-pressure mercury lamp without a filter at 308 K. Products were analyzed with a Shimadzu GC-3BT gas-chromatograph (bis(2-methoxyethyl) adipate column, 6 m, 338 K).

2.4. ESR measurements

The pre-treatment is as follows: the composite oxide (ca. 100 mg) in an ESR tube was heated in an O_2 atmosphere (8 kPa) at 473 K for an hour followed by evacuation at the same temperature for 2 h. After cooling to 293 K, O_2 (8 kPa) was added followed by irradiation with a high-pressure mercury lamp (HB-100, Fuji Glass Work, 100 W). Oxygen was evacuated and an ESR measurement was carried out at 293 K with JEOL TE-300 and ES-PRIT 425

spectrometers equipped with an Mn^{2+} marker and a variable temperature equipment.

TS-1 (0.22 g) in an ESR tube was heated in vacuo at 473 K for 1 h and cooled to room temperature. Ethylene (6.5 kPa) was added and the TS-1 was irradiated for 20 min at 77 K. The tube was taken out from a liquid nitrogen Dewar vessel and was allowed to stand in the atmosphere for just 30 s and dipped quickly into the Dewar vessel. Then, the tube was warmed to room temperature for 1 min. The difference spectrum between them gave a π -radical species.

After pre-treatment oxygen (4 kPa) was admitted to an ESR tube containing TiO_2 – SiO_2 (or TS-1) and irradiation was carried out at 77 K. Residual oxygen in the gas phase was evacuated and propylene (1.3 kPa) was added at 77 K. Irradiation was done again. All ESR spectra were obtained at 77 K. The irradiation period and time to be allowed to stand were described in the Figs. 5–7.

2.5. Oxygen exchange

Oxygen exchange between $^{18}\text{O}_2$ (Euriso Top Co., 1.1 kPa) and $^{16}\text{O}_2$ (1.1 kPa) was conducted under irradiation over TiO_2 – SiO_2 or TS-1 for 60 min. Purity of $^{18}\text{O}_2$ is 97.5%. Masses were measured by an Ulvac MSG-150A Q-mass spectrometer.

3. Results and discussion

3.1. UV–VIS absorption spectra of TiO_2 – SiO_2

XAFS and ESR measurements showed that Ti sites in less than 10 mol% TiO_2 – SiO_2 composite oxides were of tetrahedral configuration, while those with higher Ti content were of octahedral one [1–3].

UV–VIS diffuse reflection spectroscopy was done for TiO_2 – SiO_2 composite oxides (Fig. 1). The lowest absorption wavelength (265 nm) was observed for 2 mol% TiO_2 . Absorption bands are shifted to longer wavelengths with the increase in Ti content. A similar trend was observed for TiO_2 – SiO_2 prepared by a sol–gel method [9]. A jump of maximum absorption band was observed at 30 mol% of TiO_2 . Crystal growth of TiO_2 occurs above 30 mol% of TiO_2 . The absorption band was observed at 210 nm for TS-1,

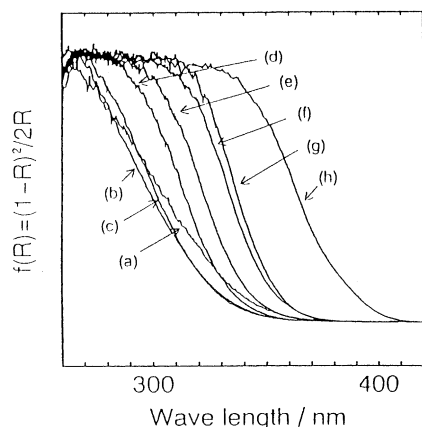


Fig. 1. UV-VIS spectra of $\text{TiO}_2\text{-SiO}_2$ prepared by rapid hydrolysis. Ti mol%: (a) 2; (b) 5; (c) 30; (d) 40; (e) 50; (f) 60; (g) 75; (h) 100.

which is in accordance with the band at 220 nm reported by Khouw et al. [10]. The band was assigned to the isolated framework Ti in a tetrahedral coordination [11,12]. There have also been observed different behavior between two Ti sites: the ESR signal of O_2^- species (3.3. [13]) and the IR band at 960 cm^{-1} were observed only for TS-1 [14]. An explanation is that titanium located in a matrix of silica is forced to be strained and gives a shift of the absorption band. The spectroscopic difference of UV-VIS absorption between Ti sites reflects the difference in photooxidation of propylene described in Section 3.2. DR UV-VIS spectroscopy is not sensitive for the discrimination of tetrahedral structure of Ti sites.

3.2. Photooxidation of propylene

Photooxidation of propylene was carried out with 5/95 and 75/25 $\text{TiO}_2\text{-SiO}_2$ composite oxides and TS-1 (Table 1). There is much difference in the reactivity among three catalysts. Since Ti content in TS-1 is 2 mol%, the reactivity of TS-1 is much higher than that of 5/95 $\text{TiO}_2\text{-SiO}_2$. This is because most of TiO_2 in TS-1 are active for the photooxidation, and considerable amounts of TiO_2 in the $\text{TiO}_2\text{-SiO}_2$ composite remained in the bulk to be inactive, which is a demerit for the photooxidation catalyst.

Propylene oxide was produced in the photooxidation of propylene over 5/95 $\text{TiO}_2\text{-SiO}_2$ and TS-1. No epoxide was formed on 75/25 $\text{TiO}_2\text{-SiO}_2$. Ohno et al.

Table 1
Photooxidation of propylene^a

Product	Composition (%)		
	5/95 $\text{TiO}_2\text{-SiO}_2$	75/25 $\text{TiO}_2\text{-SiO}_2$	TS-1
Conversion	10.3	13.2	10.9
Propylene oxide	14.8	Trace	15.1
CH_3COCH_3	11.0	2.5	22.6
CH_3CHO	13.0	4.0	19.2
$\text{CH}_3\text{CH(OH)CH}_3$	Trace	11.5	Trace
CO_2	61.2	82.0	43.0

^a Reaction conditions: C_3H_6 : 260 μmol ; $\text{O}_2/\text{C}_3\text{H}_6$: 3; reaction time: 24 h (5/95); 1 h (75/25); 2 h (TS-1).

carried out the liquid-solid phase photo-epoxidation of hexenes over TiO_2 powder [4]. We carried out propylene photooxidation in the gas-solid phase. The structure of Ti sites in 75/25 $\text{TiO}_2\text{-SiO}_2$ is almost the same as that of anatase TiO_2 [1]. The discrepancy in epoxide formation may come from the different reaction phase and the different substrate.

The 2-propanol was only formed with 75/25 $\text{TiO}_2\text{-SiO}_2$. Its formation might be due to the photoreduction of acetone with water [15] rather than hydration of propylene. The different Ti sites lead to different products in the photooxidation of propylene. Epoxide formation was produced by the catalysis of tetrahedral titanium sites.

Complete combustion occurred over all catalysts tested. Acetaldehyde, propylene oxide and acetone are produced by the monooxygen addition. A considerable amount of CO_2 were produced not only by the direct photooxidation of propylene, but also the successive photooxidation of oxygenated products. We observed that photooxidation of acetone gave completely CO_2 in conversions of 36 (360 min), 51 (30 min), and 2% (20 min) over 5/95, 75/25 $\text{TiO}_2\text{-SiO}_2$, TS-1, respectively.

3.3. Photoactive species on Ti sites

The g_1 values of O_2^- formed on pre-heated $\text{TiO}_2\text{-SiO}_2$ composite oxides vary with the Ti content [3]. Table 2 shows anisotropic g values of O_2^- produced by irradiation on $\text{TiO}_2\text{-SiO}_2$ at 293 K in the presence of O_2 . These values are a little higher than those of O_2^- formed on pre-heated TiO_2 [3], but the g_1 values similarly vary with the Ti content (Fig. 2).

Table 2
ESR data of O_2^- produced by irradiation in O_2 (measured at 293 K)

Ti content (mol%)	g_1	g_2	g_3
5	2.0220	2.010	2.003
10	2.0218	2.010	2.003
20	2.0217	2.010	2.003
30	2.0212	2.010	2.003
50	2.0204	2.010	2.003
75	2.0193	2.010	2.003
TS-1 ^a	2.0229	2.010	2.003

^a Another peak was observed at $g = 2.0283$.

It is worth noting that ESR signals of O_2^- produced by irradiation gave one more peak in the lower magnetic field at 77 K (Fig. 3). It may be assumed that the signal at the higher g value is O_2^- on a tetrahedral Ti site and that at the lower g value is O_2^- on octahedral TiO_2 . However, two signals appeared at 2.0274 and 2.0224 for 5/95 TiO_2-SiO_2 .

We observed in a separate experiment that TS-1 gave two signals ($g = 2.0283, 2.0229$) in the lower magnetic field at 293 K (Table 2). But at 77 K, only the signal at $g = 2.0283$ was remained. On the other hand, g_1 signals of O_2^- on 20–50 mol% TiO_2-SiO_2 were split into two signals at 77 K. The higher g_1 peak at $g = 2.0267$ diminished and the peak at $g = 2.0218$ became greater with the increase in Ti content. Two signals of 5–10 mol% TiO_2-SiO_2 was shifted to lower magnetic field. However, the signal of higher g values is not predominant. It can be deduced that though tetrahedral Ti sites were observed in low loaded TiO_2-SiO_2

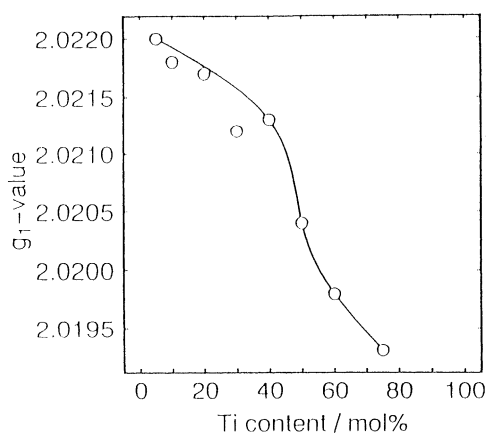


Fig. 2. Plot of g_1 values of O_2^- (measured at 293 K) vs. Ti content in TiO_2-SiO_2 .

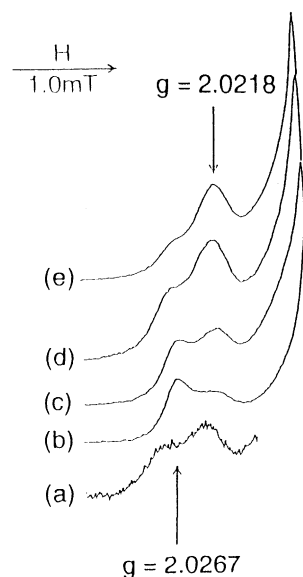
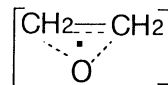


Fig. 3. The g_1 regions in ESR spectra of O_2^- (measured at 77 K) on TiO_2-SiO_2 irradiated at 77 K. Ti mol%: (a) 10; (b) 20; (c) 30; (d) 40; (e) 50.

from XAFS and ESR spectroscopy [1,3], the environment of the tetrahedral Ti sites of 5/95 TiO_2-SiO_2 is different from that of tetrahedral Ti sites of TS-1. ESR signals of g_1 values of O_2^- species on TiO_2-SiO_2 at 293 K are more sensitive for the discrimination of their micro-structures than those at 77 K.

Since a complicated spectrum is expected from propylene having non-equivalent olefinic hydrogen, ethylene was used for the detection of photoactive species on TiO_2 . Ethylene (6.5 kPa) was added to TS-1 at 293 K and irradiation was carried out at 77 K for 20 min. The ESR tube was taken out from a liquid nitrogen Dewar vessel into the atmosphere for just 30 s and dipped quickly into the vessel. Then, the tube was warmed to room temperature for 1 min and cooled to 77 K. The ESR difference spectrum between allowing to stand the tube for 30 s and 1 min is shown in Fig. 4. The quintet lines which disappeared on prolonged warming were observed at $g = 2.000$ with $A = 1.89$ mT. The signal can be assigned as a bridged π -conjugated species similar to the C_2H_4O radical formed on $MoO_3/Vycor$ glass [16].



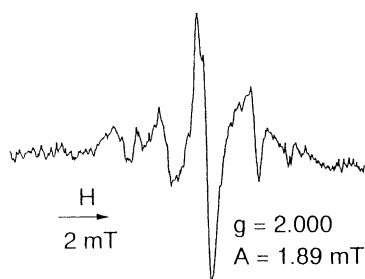
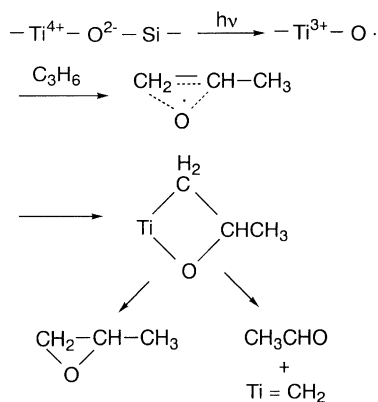


Fig. 4. The ESR difference spectrum giving a radical involving ethylene (see in the text).

The detection of the π -radical from the difference spectra indicates that the π -radical should be produced from O^- species on photoactivated TiO_2 and ethylene, and was unstable to be present at room temperature. The O^- species were expected to be observed at 77 K, but we could not detect them at the temperature. Similar π -radicals have failed to be detected on 5/95 and 75/25 TiO_2 - SiO_2 .

Irradiation of less than 350 nm light causes excitation of Ti-O bond into $(Ti^{3+}-O^-)$ [17] which reacts with propylene to form a π -radical. The intermediate π -radical leads to a titanaoxacyclobutane by the interaction between a coordinately unsaturated titanium and terminal olefinic carbon atom. Propylene oxide is formed by reductive elimination via C-O bond formation, and acetaldehyde via simultaneous C-C and Ti-O bond fission as shown in Scheme 1.

Metallaoxacyclobutane has been postulated as a reactive intermediate for epoxidation [18]. The generation of Ti-C bond requires a coordinately unsaturated



Scheme 1.

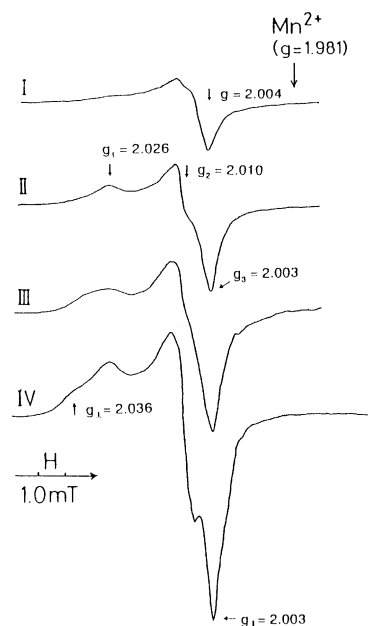


Fig. 5. ESR spectra of 5/95 TiO_2 - SiO_2 (77 K): (I) after irradiation in O_2 (10 min); (II) propylene (1.3 kPa) added to (I); (III) after irradiation (10 min) in $C_3H_6-O_2$; (IV) further irradiation (20 min). The spectrum is reduced by a factor of 1/4.5.

Ti site. Propylene is recovered by simultaneous splitting of C-O and Ti-C bonds, that is, the reverse reaction.

Irradiation on TiO_2 - SiO_2 and TS-1 was conducted in O_2 and propylene at 77 K. The reactions were traced by an ESR technique (Figs. 5–7). The ESR spectra of 5/95 TiO_2 - SiO_2 are very similar to those of TS-1 with less intensity, but are quite different from those of 75/25 TiO_2 - SiO_2 . The less intensity of the ESR spectra of 5/95 TiO_2 - SiO_2 is responsible for the failure of detection of π -radical species from ethylene.

When irradiation was carried out in O_2 , O_2^- and F centers ($g = 2.004$) [19] were observed (Figs. 5 and 6(I)). The addition of propylene without irradiation increased the intensity of O_2^- signals and decreased the intensity of F centers (Figs. 5 and 6(II)). It is known that O_2^- is also formed from F centers in the following reaction [20].



Epoxidation of olefins with oxygen by $Ni(acac)_2$ proceeds in the presence of aldehyde [21]. A ternary

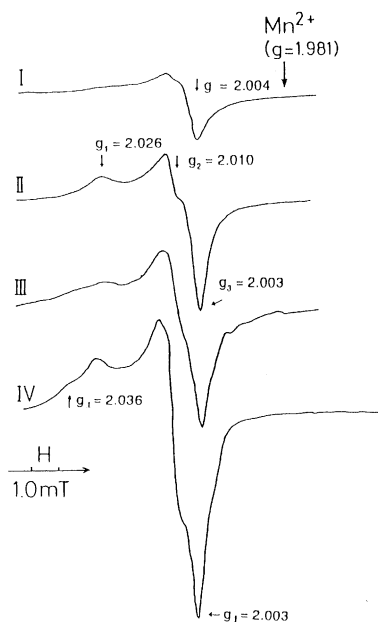


Fig. 6. ESR spectra of TS-1 (77 K): (I) after irradiation in O₂ (10 min); (II) propylene (1.3 kPa) added to (I); (III) after irradiation (10 min) in C₃H₆-O₂; (IV) further irradiation (20 min). The total spectrum is reduced by a factor of 1/2.2.

complex including Ni complex, O₂ and aldehyde was postulated as an intermediate for epoxidation. The enhancement of O₂⁻ signals by the addition of propylene is assumed to be due to the complex formation of the similar ternary complex composed of F center of TiO₂, propylene and O₂.

No Ti³⁺ signals were formed on prolonged irradiation. Instead signals at g_⊥ = 2.036 and g_∥ = 2.003 became pronounced (Figs. 5 and 6(III and IV)). These can be assigned as 2-propoxy radical from the similar g value of ethoxy radical [22]. Since the 2-propoxy radical was not observed in the absence of oxygen (Fig. 4), oxygen in the 2-propoxy radical should be derived from O₂. Acetone was produced via 2-propoxy radical as was postulated in the photo-oxidation of 2-propanol over TiO₂ [23].

Similarly O₂⁻ species were formed during irradiation on 75/25 TiO₂-SiO₂ in O₂ (Fig. 7(I)). A new signal at g = 2.014 is assigned as O₃⁻ as was observed in the literature [24,25]. It comes from the following reaction.

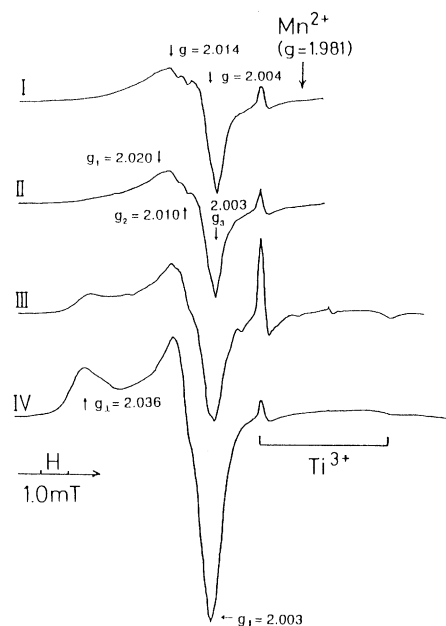
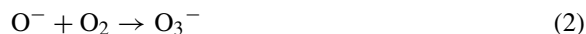
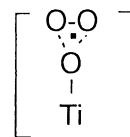


Fig. 7. ESR spectra of 75/25 TiO₂-SiO₂ (77 K): (I) after irradiation in O₂ (1 min); (II) propylene (1.3 kPa) added to (I); (III) after irradiation (0.5 min); (IV) further irradiation (3 min). The spectrum is reduced by a factor of 1/14.

Since Ti-O-Ti bonds are more abundant than Ti-O-Si, O⁻ is originated from Ti-O-Ti. Oxygen exchanges between ¹⁸O₂-¹⁶O₂ and ¹⁸O₂-Ti¹⁶O₂ were conducted over photoactivated TiO₂-SiO₂ and TS-1. The extent of scrambling was in the order 75/25 TiO₂-SiO₂ > TS-1 > 5/95 TiO₂-SiO₂, in accordance with the numbers of Ti-O bonds and photoactive Ti species. This led us to assume the O₃⁻ species as the following structure judging from the result reported by Tanaka [26].



Contrary to the cases of 5/95 TiO₂-SiO₂ and TS-1, no enhancement of O₂⁻ signals was observed on 75/25 TiO₂-SiO₂ by the addition of propylene (Fig. 7(II)). Irradiation in the mixture of O₂ and propylene gave a 2-propoxy radical and Ti³⁺ species (Fig. 7(III)). The bulk of TiO₂ is more susceptible to reduction with light than dispersed TiO₂ in 5/95 TiO₂-SiO₂

and TS-1. On continuing irradiation the spectrum was covered with the enlarged signal of the 2-propoxy radical (Fig. 7(IV)). It is ascertained that acetone is produced from the 2-propoxy radical as reported by Bickley [20]. Photooxidation of acetone over three catalysts gave only carbon dioxide. A large amount of carbon dioxide produced over 75/25 TiO₂–SiO₂ was also derived from the photooxidation of acetone produced.

4. Conclusion

Propylene oxide was produced by photooxidation of propylene in the presence of oxygen over 5/95 TiO₂–SiO₂ and TS-1. However, no formation of propylene oxide occurred over 75/25 TiO₂–SiO₂. It was postulated that propylene oxide was produced by a reductive coupling of C–O bond in a titanaoxacyclobutane formed from O[−] species on tetrahedral Ti sites and propylene. The 2-propoxy radical formed from O₂[−] or O₃[−] and propylene gave acetone which was further photooxidized to carbon dioxide and water.

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