JOURNAL OF CATALYSIS 155, 196–203 (1995)

Photooxidation of Propane over Alkali-Ion-Modified V_2O_5/SiO_2 Catalysts

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Received May 16, 1994; revised March 1, 1995

Silica-supported vanadium oxides modified by alkali ions (Na^+, K^+, or Rb^+) comprise two types of surface active species, which have been elucidated by phosphorescent emission and excitation spectra and the results of photoadsorption of gaseous propane and oxygen. One is the same as that on V_2O_5/SiO_2 excited by light with wavelengths $310 < \lambda < 390$ nm and the other is that interacting with alkali ions excited by light with wavelengths $\lambda > 390$ nm. Propanone is selectively formed by the photooxidation of propane over alkali-ion-modified catalysts. The active species excited by the light of wavelengths $\lambda > 390$ nm have been found to be effective for the activation of the secondary C–H bonds of propane.

INTRODUCTION

The selective conversion of light alkanes is of current interest from both scientific and industrial viewpoints because of difficulty in activating saturated C–H bonds and the abundant resources of liquefied petroleum gas (LPG) containing mainly propane and butanes. With regard to this, oxidative dehydrogenation of propane to produce propene (1, 2) and aromatization of propane (3) have been investigated widely. It has been attempted to synthesize butenes and butadiene from *n*-butane over V–Mg–O catalysts (2, 4) and maleic anhydride from *n*-butane over V–P–O catalysts (5). In these reactions, high temperatures are very often required even at low conversion levels. On the other hand, the reactions using photocatalysts take place under mild conditions and can be controlled easily (6–9). However, there have been a few papers on photooxidation (10) and most of them report low activity and/or low selectivity to partial oxidation.

Among the photocatalysts, V_2O_5/SiO_2 is known to be effective for selective photooxidation of olefins and alcohols (7, 8). We have already reported photooxidation of propene over V_2O_5/SiO_2 and Na^+-ion-modified V_2O_5/SiO_2 (11) and discussed the promoting effect of sodium ions. Oxidative cleavage of a C=C bond is dominant over irradiated V_2O_5/SiO_2 to form ethanal, while over Na^+-ion-modified V_2O_5/SiO_2 the formation of acraldehyde is preferred. The addition of sodium ions to V_2O_5/SiO_2 brings about a reduction in the acidity of the catalyst as well as the formation of different surface vanadate species, which actively attack C–H bonds. Therefore, we expect that alkali-ion-modified V_2O_5/SiO_2 catalysts activate a C–H bond rather than a C–C bond and that light alkanes can be converted into more valuable C3 compounds over these types of catalysts. In the present paper, we report the highly selective formation of propanone from propane by photooxidation over a series of V_2O_5/SiO_2 catalysts modified by Na^+, K^+, and Rb^+ ions and discuss the photochemical properties and surface active sites formed in these catalysts.

EXPERIMENTAL

Materials. Reactants (propane and oxygen), tetraethyl orthosilicate (TEOS), ammonium metavanadate, NaOH, KOH, and RbOH were commercially supplied. Gaseous reactants were purified several times by vacuum distillation at low temperatures. $^{18}O_2$ was supplied from CEA-SEN Saclay (purity 99.88%) and used without further purification. Silica was prepared by hydrolysis of distilled TEOS and calcination at 773 K for 5 h as described elsewhere (12). The specific surface area of SiO_2 was estimated by the BET method to be 588 $m^2\ g^{-1}$.

Catalysts. V_2O_5/SiO_2 (VS; V_2O_5 2.5 wt%) was prepared by impregnating SiO_2 with an aqueous solution of ammonium metavanadate in the same manner as in (12). The specific surface area of VS was measured to be 465 $m^2\ g^{-1}$. Alkali-ion-modified V_2O_5/SiO_2 catalysts (Na–VS, K–VS, and Rb–VS) were prepared by impregnating VS with aqueous solutions of NaOH, KOH, or RbOH containing the desired amounts of Na^+, K^+, or Rb^+, respectively, followed by calcination in a dry air stream at 773 K for 5 h. The contents of alkali ions are 1, 2, and 4 wt% as Na_2O, K_2O, and Rb_2O, respectively. The specific

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surface areas of Na–VS, K–VS, and Rb–VS were estimated to be 261, 165, and 170 m^2 g^{-1}, respectively.

Pretreatment of the catalysts. Before each run and measurement, the catalyst surface was conditioned by evacuation at 673 K for 1 h, treatment with 60 Torr (1 Torr = 133.3 Pa) of oxygen gas at 673 K for 2 h, and evacuation at 673 K for 10 min, successively.

Reactions. The reactions were performed in a conventional closed circulating system (dead space 280 cm^3) described elsewhere (13, 14). The powder catalyst (500 mg) was spread on the flat bottom of a quartz reactor and irradiated with UV light at room temperature from a 250-W ultrahigh-pressure Hg lamp through UV-31 or UV-39 glass filters, which transmit light with wavelength $\lambda > 310$ nm or $\lambda > 390$ nm, respectively. The experiments were repeated multiple times to examine reproducibility of data. In the dark, the reactions did not take place. After each run, the catalyst bed was heated to 573 K to collect products which were tightly adsorbed onto the catalyst at room temperature. The desorbed products were frozen out in a trap cooled by liquid nitrogen and analyzed by GLC and GC mass spectrometry. In order to measure quantum yields in reactions of propane, the wavelengths of the irradiating light were selected by a monochromator and the intensity was calibrated by the method of chemical actinometry using potassium ferrioxalate developed by Hatchard and Parker (15).

Adsorption experiments. Photoadsorption and photodesorption of propane and oxygen were investigated using an apparatus composed of a small quartz vessel (15 ml) and a calibrated Pirani gauge (16).

Photoluminescence. Phosphorescent emission and excitation spectra for the catalysts were recorded with a Hitachi F-3010 fluorescence spectrometer (17).

RESULTS AND DISCUSSION

Photoluminescence. Figure 1 shows phosphorescence spectra of VS, Na–VS, K–VS, and Rb–VS excited at 310 nm at 77 K. The phosphorescence spectrum of VS exhibits fine structure due to V=O vibration as reported by Kazansky *et al.* (18) and Anpo *et al.* (19). The phosphorescence is attributed to the singlet–triplet charge-transfer transition of V=O in the surface tetrahedral complexes of vanadium species (VO_4^{3-}) (20). By addition of alkali ions, the intensity of the vibrational fine structure decreased and a shoulder peak was seen at the vicinity of 550 nm. In order to make this change clear, we differentiated the spectra, and the obtained first derivative curves are shown in Fig. 2. Oscillatory signals are found at the same position although the intensity gets weaker with an increase in atomic number of added alkali ions. The presence of another band centered at 550 nm becomes clearer, especially for K–VS and Rb–VS; i.e., oscillatory peaks overlap with the smooth and broad signals which have an inflection point at 550 nm. These results show that phosphorescent emission spectra of alkali-ion-modified V_2O_5/SiO_2 catalysts excited at 310 nm consist of the two kinds of emission bands; i.e., one is due to VO_4^{3-} and the other is that resulting from addition of alkali ions. Figure 3 shows excitation spectra of VS, Na–VS, K–VS, and Rb–VS monitored by 530 nm at room temperature. An absorption band centered at around 390 nm was seen in excitation spectra of K–VS and Rb–VS, suggesting the formation of a new type of species. Figure 4 shows phosphorescence spectra of VS, Na–VS, K–VS, and Rb–VS excited by 400 nm light at 77 K. Phosphorescent emission

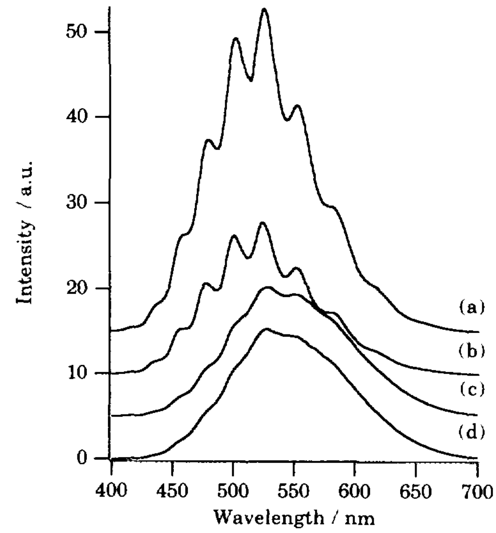

FIG. 1. Photoluminescent emission spectra excited by 310 nm light at 77 K. (a) VS, (b) Na–VS, (c) K–VS, and (d) Rb–VS.

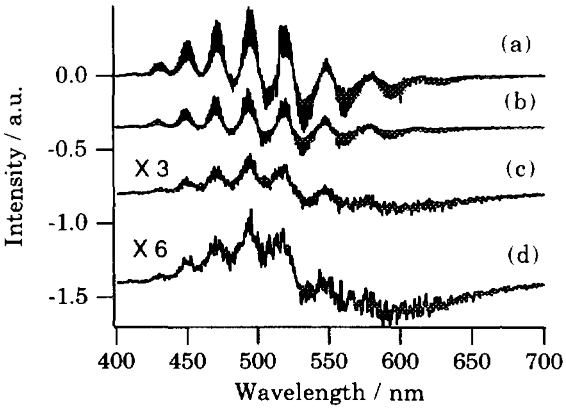

FIG. 2. The first derivative spectra of photoluminescent emission excited by 310 nm light at 77 K. (a–d) See legend to Fig. 1. × *n* stands for *n*-fold amplification in recording.

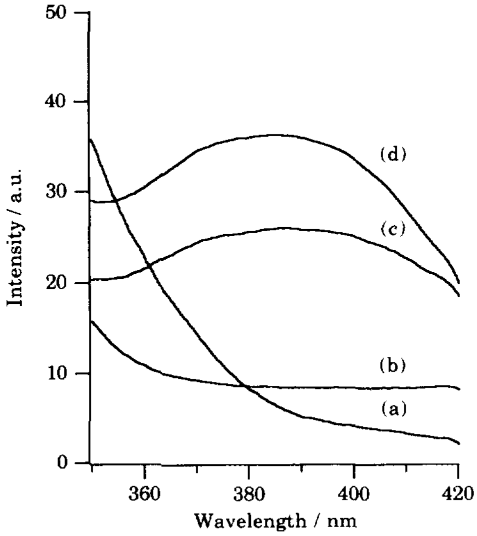

FIG. 3. Photoluminescent excitation spectra. Emission was monitored at 530 nm at room temperature. (a–d) See legend to Fig. 1.

was clearly observed for alkali-ion-modified V_2O_5/SiO_2 catalysts excited by 400 nm light and the intensity of phosphorescent emission became larger with increase in atomic number of alkali ions. From these results, we guess that addition of alkali ions to VS brings about the formation of a luminescence center different from that on VS and which is excited by light of wavelengths $\lambda > 390$ nm. Kazansky *et al.* have already reported that the Na^+-modified V_2O_5/SiO_2 catalyst has two different centers of luminescence; one is the center coinciding with that of VS, the other is that exhibiting the emission spectrum with no vibrational fine structure (21). They showed that the excitation spectrum of phosphorescence of Na^+-modified V_2O_5/SiO_2 catalyst contains two maxima. They concluded that introduction of sodium ions into VS catalyst leads to the appearance of nontetrahedral surface complexes of vanadium. Since we did not observe two maxima, we cannot affirm that the luminescence center reported in this paper is the same as that reported by Kazansky *et al.* We have already reported the preferential formation of VO_4^{3-} species on VS by Na^+ addition as revealed by XAFS spectroscopy (22). Hence, the conclusion drawn by Kazansky *et al.* that the local structure of Na^+-interacting species is not tetrahedral is very doubtful. The investigation of the local structure of the new species is now in progress.

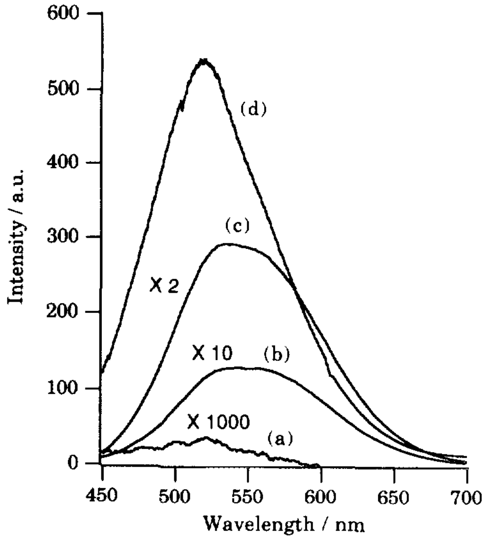

FIG. 4. Photoluminescent emission spectra excited by 400 nm light at 77 K. (a–d) See legend to Fig. 1. X*n*, see legend to Fig. 2.

In order to examine interaction between propane molecules and the luminescence center that is different from that of VS, we recorded phosphorescence spectra of Rb–VS in contact with a small amount of propane at room temperature. The phosphorescence excited by 400-nm light was quenched efficiently and evacuation of gaseous propane for 1 min did not cause recovery of phosphorescence. This result indicates that the quenching was not caused by physical collision of propane molecules with the luminescence sites but by some chemical interaction of propane molecules.

Adsorption experiments. In order to investigate the interaction between propane and the surface of the catalysts, we carried out adsorption experiments at a low pressure (ca. 0.2 Torr) to suppress the further reaction as much as possible. The first 40-min part of Fig. 5 shows the pressure change of propane in contact with VS catalyst. In the dark as well as under irradiation through UV-39, no adsorption was observed. However, under irradiation through UV-31, a drastic pressure decrease was observed and no desorption was observed even after the irradiation ceased. This indicates that propane was chemically photoadsorbed on VS excited by light of wave-

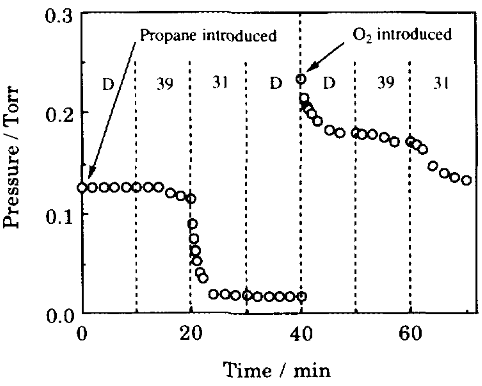

FIG. 5. Change in the pressure of propane and oxygen following UV irradiation over VS. D, in the dark; 31, UV irradiation through UV-31; 39, UV irradiation through UV-39; see text.

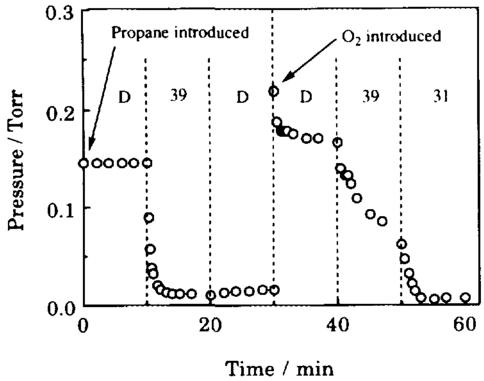

FIG. 6. Change in the pressure of propane and oxygen following UV irradiation over K–VS. D, 31, and 39, see legend to Fig. 5.

lengths $310 < \lambda < 390$ nm. This is the same as our earlier observation for photoadsorption of propene in contact with VS catalyst (16).

The first 30-min part of Fig. 6 shows the pressure change of propane in contact with K–VS catalyst. In the dark, no adsorption occurred. However, a drastic pressure decrease was found by irradiation through UV-39 in this case. The same phenomena were observed for Na–VS and Rb–VS catalysts.

Anpo *et al.* reported that photooxidation of CO is associated with the excited triplet states of V=O in V_2O_5 supported on porous vycor glass excited by 300 nm light (19). We also reported that the active site of photooxidation of propene and CO on VS is the V=O bond excited by irradiation of the light of wavelengths 310–390 nm (16). In the present case, it is likely that the active site on VS is the same species. On the other hand, the adsorption of propane with irradiation through UV-39 on alkali-ion-modified V_2O_5/SiO_2 suggests the presence of active species different from VS. From the results of photoadsorption of propane and phosphorescence spectra, we conclude that luminescence sites arising from addition of alkali ions excited by the light of the wavelengths $\lambda > 390$ nm interact with propane molecules.

Desorption of propane was not observed for any samples after ceasing irradiation. The present results suggest strong interaction between propane and the excited surface and the formation of stable complexes on the surface as reported for the case of adsorption of propene on VS (16, 23).

No appreciable photoadsorption of oxygen was observed on bare VS and the alkali-ion-modified catalysts; however, the catalysts preadsorbing propane were found to cause the photoadsorption of oxygen as shown in Figs. 5 and 6 after the 40- and 30-min regions, respectively. Oxygen was introduced into the vessel, following to the propane photoadsorption experiment and evacuation of gaseous propane for 10 s. Over VS, photoirradiation through UV-39 caused only a small pressure change, but irradiation through UV-31 caused an appreciable pressure change by adsorption. Taking into account the results for propane adsorption experiments, this shows that the effective wavelengths for adsorption is in the range of 310–390 nm for VS. On the other hand, over K–VS, photoirradiation through UV-39 caused a drastic pressure decrease. The same phenomena were observed for Na–VS and Rb–VS. This shows that for alkali-ion-modified V_2O_5/SiO_2 catalysts the effective wavelengths λ for the adsorption extends to the range of $\lambda > 390$ nm, as found in the case of propane adsorption. Since only the catalyst preadsorbing propane caused photoadsorption of oxygen, it is likely that photooxidation of propane is initiated by the activation of propane on photoexcited catalysts.

Reactions. Table 1 shows the results of photooxidation of propane by irradiation by the light of wavelengths $\lambda > 310$ nm. The products were propene, propanal, propanone, ethanal, and others. It is noted that activity for oxidation is much higher for alkali-ion-modified catalysts

TABLE 1

Photooxidation of Propane over V_2O_5/SiO_2 and Alkali-Ion-Modified V_2O_5/SiO_2 Catalysts under Irradiation by the Light of Wavelengths $\lambda > 310$ nm[a]

Catalyst	Conv.[b] (%)	Selectivity[c] (%)						
		C_3H_6	C_2H_5CHO	$(CH_3)_2CO$	C_2H_3CHO	C_2H_4	CH_3CHO	CO_X
VS	63.4	10	12	16	1	2	17	42
Na-VS	83.8	4	1	33	0	4	2	56
K-VS	85.2	2	1	37	0	1	1	57
Rb-VS	88.5	1	0	33	0	1	1	63

[a] Catalyst 0.5 g, propane 70 μmol, O_2 140 μmol, reaction time 1 h.

[b] Based on propane.

[c] Based on converted propane. CO_X stands for CO and CO_2. The other products were propene oxide, butanone, and hexanes of trace amounts.

TABLE 2

Photoassisted Reaction of Propane in the Absence of Gaseous Oxygen over V_2O_5/SiO_2 and Alkali-Ion-Modified V_2O_5/SiO_2 Catalysts under Irradiation by the Light of Wavelengths $\lambda > 310$ nm[a]

Catalyst	Conv.[b] (%)	Selectivity[c] (%)						
		C_3H_6	C_2H_5CHO	$(CH_3)_2CO$	C_2H_3CHO	C_2H_4	CH_3CHO	CO_X
VS	11.6	80	0	4	0	6	5	5
Na–VS	15.9	80	tr	4	0	3	0	13
K–VS	15.9	91	0	2	0	1	0	0
Rb–VS	17.8	82	0	1	0	1	0	16

[a] Catalyst 0.5 g, propane 70 μmol, reaction time 1 h.

[b] Based on propane.

[c] Based on converted propane. CO_X stands for CO and CO_2.

than that for VS. On the other hand, the yield of partial oxidation products is almost the same for VS and alkali-ion-modified catalysts, indicating that over the latter catalysts, total oxidation is a predominant reaction. As for selectivity, over alkali-ion-modified catalysts, propanone was dominantly formed, while over VS catalyst, a variety of products were formed. In particular, ethanal, a product of oxidative cleavage of a C–C bond, was formed in a considerable fraction. On the other hand, over alkali-ion-modified V_2O_5/SiO_2 catalysts propanone was formed with high selectivity. The result clearly suggests that the modification by alkali ions brings about the change in the property of the surface active sites on VS.

Table 2 shows the results of the photoassisted reaction of propane in the absence of gaseous oxygen by irradiation by the light of wavelengths $\lambda > 310$ nm. The level of propane conversion was very low in the absence of gaseous oxygen. Small amounts of oxygen-containing products were formed and a main product was propene. These results suggest that insertion of an oxygen atom into propane requires gaseous oxygen.

We carried out photooxidation of propane by irradiation with light of wavelengths $\lambda > 390$ nm to investigate the role in photooxidation of species which exhibit emission by 400 nm light and act as photoadsorption sites for propane, as mentioned above. The results are given in Table 3. Photooxidation of propane over VS was much reduced under this condition, as expected by the result of adsorption experiment. In contrast, over alkali-ion-modified V_2O_5/SiO_2 catalysts, although conversion of propane decreased slightly, the yields of partial oxidation products increased in comparison with the yields from the reactions under irradiation through UV-31. As for selectivity, propanone increased and CO_x decreased compared with those for the reactions by irradiation by light of wavelengths $\lambda > 310$ nm. This indicates that the reaction paths to CO and CO_2 formation are suppressed. We suppose that active sites different from VS are generated by addition of alkali ions to V_2O_5/SiO_2 and that active species on both the catalysts excited by 310 to 390-nm light promote C–C bond fission and unselective activation of the C–H bond. The active species on alkali-ion-modified V_2O_5/SiO_2 excited by the light of longer wavelengths are responsible for secondary C–H bond activation.

TABLE 3

Photooxidation of Propane over V_2O_5/SiO_2 and Alkali-Ion-Modified V_2O_5/SiO_2 Catalysts under Irradiation by the Light of Wavelengths $\lambda > 390$ nm[a]

Catalyst	Conv.[b] (%)	Selectivity[c] (%)						
		C_3H_6	C_2H_5CHO	$(CH_3)_2CO$	C_2H_3CHO	C_2H_4	CH_3CHO	CO_X
VS	5.0	43	19	15	0	tr	13	9
Na–VS	60.3	8	7	52	0	1	7	25
K–VS	67.0	4	2	51	0	1	3	39
Rb–VS	67.1	3	1	60	0	1	1	34

[a] Catalyst 0.5 g, propane 70 μmol, O_2 140 μmol, reaction time 1 h.

[b] Based on propane.

[c] Based on converted propane. CO_X stands for CO and CO_2. The other products were propene oxide, butanone, and hexanes of trace amounts.

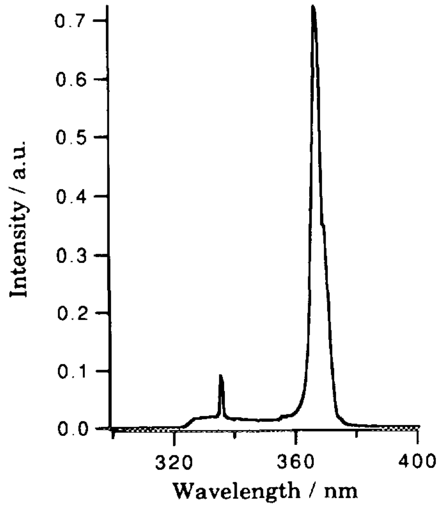

FIG. 7. Distribution of monochromatized light.

We carried out photooxidation of propane over Rb–VS by irradiation by the light through monochromator in order to investigate the quantum yield in the reaction. Figure 7 shows the distribution of monochromatized light. The amounts of photons determined by the method of chemical actinometry were 1.9×10^{-8} mol/s. The quantum yield was estimated as 0.08, assuming that one molecule of propane is converted into products by one photon. The quantum yield was regarded as the lowest value in view of the loss of light intensity due to scattering by the catalyst.

Active oxygen species in the reaction. In order to investigate active oxygen species in photoassisted oxidation of propane, we carried out the reactions with $^{18}O_2$. Figures 8 and 9 show the results of the time course of photoassisted reaction of propane over Rb–VS by irradiation by the light of wavelengths with $\lambda > 390$ nm. As shown in Fig. 8, conversion of propane increased and the rate of the reaction became sluggish with irradiation time. Figure 9 shows the contents of ^{18}O which were contained in propanone and propanal formed in the reactions. In the initial stage in the reaction, most oxygen atoms incorporated in propanone and propanal were ^{16}O atoms which originated from lattice oxygen atoms in the catalyst and the ratio of ^{18}O increased gradually with irradiation time. Taking into consideration that no reaction was observed in the dark, this result suggests that the active oxygen species is lattice oxygen excited by photons. We have already reported that lattice oxygen atoms in vanadium oxide supported on silica were exchanged for oxygen atom in propanone molecules under UV irradiation (24). However, the exchange between lattice and propanone is very slow, and we cannot suppose that the increased ^{18}O content of propanone and propanal is mainly due to the exchange. It is likely that gaseous oxygen molecules work as reagents to regenerate lattice oxygen which is incorporated into products. If this is the case, the number of active sites is limited and they participate in "catalytic" reaction. For the reasons mentioned above, we suppose that the contents of ^{18}O atoms in propanone and propanal increase with irradiation time.

Deactivation of the catalysts. In order to investigate durability of alkali-ion-modified V_2O_5/SiO_2 catalysts, we carried out successive photooxidation of 2-methylpropane over Rb–VS by irradiation by the light of wavelengths $\lambda > 390$ nm. The reactions were repeated several times without treatment of oxygen gas after each run. Figure 10 shows the change of conversion by the repeated run. The products were propanone, 2-methyl-2-propanol, 2-methylpropanal, 2-methylpropene, and others and selectivities changed little in each run. The level of conversion decreased and the catalyst changed from white to a

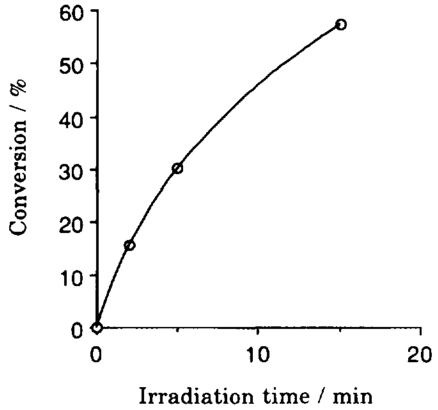

FIG. 8. Time course of conversion in photooxidation of propane with $^{18}O_2$ over Rb–VS by irradiation by the light of wavelengths $\lambda > 390$ nm. Catalyst, 0.5 g; propane, 50 μmol; $^{18}O_2$, 50 μmol.

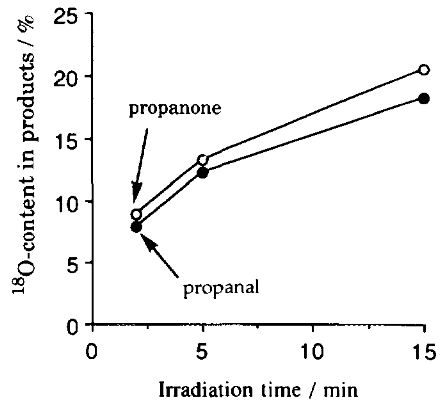

FIG. 9. Time course of ^{18}O content in products in photooxidation of propane with $^{18}O_2$ over Rb–VS by irradiation by the light of wavelengths $\lambda > 390$ nm. Catalyst, 0.5 g; propane, 50 μmol; $^{18}O_2$, 50 μmol.

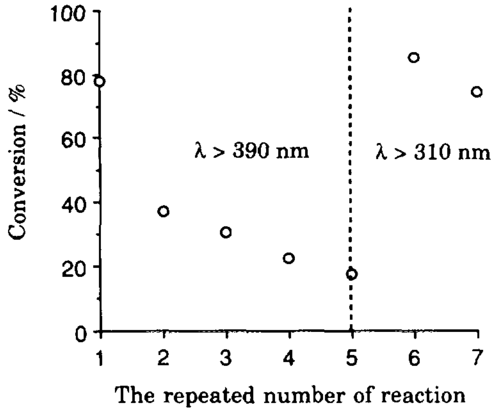

FIG. 10. Successive photooxidation of 2-methylpropane over Rb–VS catalyst. Catalyst, 0.5 g; 2-methylpropane, 42 μmol; O_2, 90 μmol; reaction time, 20 min.

darker color with increased number of repetitions. This may result from photoreduction of vanadium ions and/or coke formation on the catalyst during reactions.

After five successive runs under irradiation by light of wavelength $\lambda > 390$ nm, the next run was carried out under irradiation by light of wavelength $\lambda > 310$ nm over the same catalyst without the oxygen gas treatment. Surprisingly, the conversion level was the same as that of the fresh catalyst, as shown in Fig. 10. This clearly indicates that two kinds of active sites are present on alkali-ion-modified VS and that one was not involved in the reaction induced by irradiation with $\lambda > 390$ nm light. In addition, the total amounts of converted 2-methylpropane in all the runs were more than those of all the supported vanadium atoms and the turnover number (TON), which was defined as the number of moles of converted 2-methylpropane per mole of supported vanadium atoms, was more than 1. This TON value is the least value since all the supported vanadium atoms are assumed to be active in 2-methylpropane oxidation and this may not always be the case. From these results, photoassisted reactions of light alkanes over alkali-ion-modified V_2O_5/SiO_2 proceed catalytically and alkali-ion-modified V_2O_5/SiO_2 is highly active and selective for photocatalysts for partial oxidation of light alkanes.

CONCLUSION

From the results mentioned above, we conclude the following:

1. On alkali-ion-modified V_2O_5/SiO_2 catalysts, two kinds of luminescence center are present; one is due to VO_4^{3-} excited by 310- to 390-nm light and the other arises from addition of alkali ions, excited by light of longer wavelengths. This conclusion is supported by the results of adsorption experiments and reactions.

2. The emission centers excited by the longer wavelengths are active sites in photooxidation of propane and activate secondary C–H bonds of propane molecules selectively.

ACKNOWLEDGMENTS

We thank Dr. Segawa, Dr. Fujitsuka, and Mr. Sato of the Department of Molecular Engineering of Kyoto University for their help in measuring the light flux. The present work was partially supported by the Grant-in-Aid for Priority Area Research "Photoreaction Dynamics" from the Ministry of Education, Science, and Culture, Japan (No. 06239237).

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