Selective partial oxidation of light alkanes over alkali-ion-modified silica-supported vanadium oxides excited with visible light

Sakae Takenaka, Tsunehiro Tanaka, Takuzo Funabiki and Satohiro Yoshida

Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 606-01, Japan
E-mail: takenaka@dcc.moleng.kyoto-u.ac.jp

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Alkali-ion (Na^+, K^+, and Rb^+)-modified V_2O_5/SiO_2 irradiated with visible light catalyzes the partial oxidation of 2-methylpropane to form mainly propanone and 2-methylpropan-2-ol. The addition of alkali ions to V_2O_5/SiO_2 is essential to generate the active site that can be excited with visible light. It is confirmed that there are two types of reaction paths for the formation of 2-methylpropan-2-ol.

Keywords: partial oxidation of 2-methylpropane, alkali ions, silica-supported vanadium oxide, photocatalyst, active oxygen species

1. Introduction

Various promoters are incorporated into catalysts with a view to control activity and selectivity of the catalytic reaction and to improve thermal stability of catalysts. For example, alkali metal is often used as one of the typical modifiers for metal oxide catalysts [1]. As is well-known, one of their distinct functions is their electron-donating ability leading to the enhancement of the basicity of metal oxides. Rare earth metals are added into supported catalysts to prevent the supports such as alumina from sintering [2].

Vanadium oxide-based catalysts are extensively used for the catalytic oxidation of hydrocarbons. To achieve a good activity and selectivity level, V_2O_5 should be dispersed on a support. The improvement of activity and selectivity of supported vanadium oxide catalysts has been widely attempted by addition of alkali ions. Van Hengstum et al. [3] observed that the influence of potassium additives on V_2O_5/TiO_2 catalysts depended on the type of hydrocarbons oxidized. Potassium changed the nature of the active sites, which was attributed to the possible formation of amorphous bronzes between vanadium oxide and potassium. Rives et al. [4,5] have reported a larger selectivity for propene oxidation to acrolein on V_2O_5/TiO_2 when these catalysts are doped with alkali ions. The results obtained by XRD, DTA (differential thermal analysis), IR, TPR (temperature-programmed reduction) and XANES (X-ray absorption near-edge structure) indicate that doping V_2O_5/TiO_2 with increasing amounts of sodium ions leads initially to formation of V–Na–O compounds with a Na/V ratio close to 0.5 that are reduced at a higher temperature than V_2O_5 formed in the absence of sodium. They reported the formation of Na_3VO_4 when the amount of sodium is increased up to 3%. Wachs et al. [6] have studied the effect of addition of potassium on the structure of the surface vanadium oxide phase in V_2O_5/TiO_2 catalysts. They reported that the gradual addition of potassium to V_2O_5/TiO_2 poisons the surface vanadium redox sites. This is reflected in changes in the Raman spectra and a decrease in activity in methanol oxidation.

Silica-supported vanadium oxide catalysts are known to be active for photooxidation of CO [7,8], and alkenes [9]. However, the influence of the addition of alkali ions into supported vanadium oxide catalysts on photocatalysis has been little investigated. We have reported the effect of addition of alkali ions into V_2O_5/SiO_2 on activity and selectivity in the photooxidation of propene and propane, photoluminescence, and structure of surface vanadate [10–12]. Addition of Na^+ to V_2O_5/SiO_2 causes preferential formation of tetrahedral species, $(V{=}O)O_3$, which are active sites for photooxidation over V_2O_5/SiO_2 catalysts. In addition, two kinds of luminescence centers are present on alkali-ion-modified V_2O_5/SiO_2 catalysts. One (S 310) is due to VO_4^{3-} excited by light of 310–390 nm. The other (S 400) is that arising from addition of alkali ions, excited by irradiation by light of wavelengths $\lambda > 390$ nm. In the photooxidation of propane over alkali-ion-modified V_2O_5/SiO_2 catalysts under the conditions where only S 400 was excited, propane was converted to propanone selectively. We have also observed the formation of 2-methylpropan-2-ol in the photooxidation of 2-methylpropane over Rb^+-modified V_2O_5/SiO_2 [13]. These results suggest that S 400 is effective for activation of the C–H bond of light alkanes and it is much affected by the presence of alkali ions.

In the present paper, we report the results of photooxidation of 2-methylpropane over alkali-ion-modified V_2O_5/SiO_2 catalysts and describe activity and selectivity in these reactions to discuss the promotion effect of alkali ions. We also investigate active oxygen species for the formation of 2-methylpropan-2-ol and the factor for the formation of S 400 in alkali-ion-modified V_2O_5/SiO_2.

2. Experimental

Materials. Reactants (2-methylpropane, propane and oxygen), tetraethyl orthosilicate (TEOS), ammonium metavanadate, NaOH, KOH, KNO_3, RbOH, $Mg(NO_3)_2$, $Eu(NO_3)_3$, $Pr(NO_3)_3$, and $Ce(NO_3)_3$ were commercially supplied. Gaseous reactants were refined by vacuum distillation. $C^{18}O_2$ and $H_2{}^{18}O$ were supplied from ICON (purity 99.5%) and CEA-ORIS (purity 98.1%), respectively, and used without further purification. Silica was prepared by the hydrolysis of distilled TEOS and calcination at 773 K for 5 h as described elsewhere [14].

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 matavanadate in the same manner as given in ref. [14]. Modified VS catalysts were prepared by impregnating VS with aqueous solutions of NaOH (Na-VS), KOH (K-VS), KNO_3 (Kn-VS), RbOH (Rb-VS), $Mg(NO_3)_2$ (Mg-VS), $Eu(NO_3)_3$ (Eu-VS), $Pr(NO_3)_3$ (Pr-VS), or $Ce(NO_3)_3$ (Ce-VS).

Pretreatment of the catalysts. Pretreatment of the catalysts was performed first by evacuation at 673 K for 1 h, then treatment with 60 Torr of oxygen at the same temperature for 2 h and evacuation at the same temperature for 10 min prior to reaction and measurement of each spectrum.

Reactions. Reactions were carried out in a conventional closed gas-circulating system (dead space 280 cm^3) described elsewhere [14]. The powder catalyst (500 mg) was spread on the flat-bottom of a quartz reactor and irradiated at room temperature by light from a 250 W ultra-high-pressure Hg lamp through glass filters, UV-31 or UV-39, which permit light with wavelength $\lambda > 310$ nm or $\lambda > 390$ nm, respectively. The experiments were repeated more than twice to examine the reproducibility of data. In the dark, the reactions did not take place. After each run, the catalyst bed was heated to 573 K for collecting products which were tightly adsorbed on the catalyst at room temperature. The desorbed products were frozen out in a trap cooled by liquid nitrogen, and analyzed by GLC and GLC–mass spectrometry. In order to measure quantum yields in reactions of 2-methylpropane, 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].

Photoluminescence. Phosphorescent emission spectra of the catalysts were recorded with a Hitachi F-3010 fluorescence spectrometer [16].

3. Results and discussion

3.1. Reactions

Table 1 shows the results of the photooxidation of 2-methylpropane over VS and alkali-ion-modified VS catalysts by irradiation with light of wavelengths $\lambda > 310$ nm. Both the active sites (S 310 and S 400) were excited under this condition. Over VS, a variety of products, for example, propanone, ethanal, 2-methylpropanal, 2-methylpropene and so on, were formed. This indicates that nonselective activation of C–H bonds in 2-methylpropane takes place over VS. On the other hand, the formation of products, except for propanone, was suppressed, whereas selectivity to propanone increased considerably over alkali-ion-modified VS catalysts. In spite of the higher conversion level over alkali-ion-modified catalysts than over VS, the selectivity to COx was almost of the same level over all the catalysts. In addition, formation of 2-methylpropan-2-ol was detected

Table 1
Photooxidation of 2-methylpropane over VS and alkali-ion-modified VS catalysts by irradiation by light of wavelengths $\lambda > 310$ nm [a]

Catalysts [b]	Conv. [c] (%)	Selectivity [d] (%)							
		IB	PR	AA	AC	TB	BA	ML	COx
VS [e]	58.4	8	6	10	36	0	9	1	29
Na-VS	84.6	7	1	2	41	1	3	1	39
K-VS	90.7	6	1	2	51	5	2	1	31
Rb-VS [e]	94.3	6	1	1	51	5	3	1	31

[a] Catalyst 0.5 g, 2-methylpropane 70 μmol, O_2 140 μmol, irradiation time 60 min.

[b] The contents of alkali-ion are 1, 2, or 4 wt% as Na_2O, K_2O, or Rb_2O, respectively.

[c] Based on introduced 2-methylpropane.

[d] Based on converted 2-methylpropane. IB 2-methylpropene, PR propene, AA ethanal, AC propanone, TB 2-methylpropan-2-ol, BA 2-methylpropanal, ML methacrolein, COx CO and CO_2. Trace amounts of methanol, ethene, propene oxide, propanal, propan-2-ol, and 2-methylpropanol were formed.

[e] Taken from ref. [13].

over only alkali-ion-modified catalysts. These results suggested that modification by alkali ions brought about high activity and selectivity to partial oxidation of 2-methylpropane.

In order to investigate the difference of the reactivity between S 400 in alkali-ion-modified catalysts and S 310 in all the catalysts, we carried out the reactions by irradiation by light of wavelengths $\lambda > 390$ nm. Only S 400 was excited under this condition. The results are given in table 2. The VS catalyst was almost inactive because of the absence of S 400. In contrast, the reactions did proceed over all the alkali-ion-modified catalysts and the conversion levels were very high, indicating that S 400 is active for oxidation of 2-methylpropane. As for selectivity, COx decreased considerably, and C_4-compounds, in particular 2-methylpropan-2-ol increased in comparison with the reactions over alkali-ion-modified catalysts irradiated by light of wavelengths $\lambda > 310$ nm. These results demonstrate that S 400 excited by light of wavelengths $\lambda > 390$ nm activates the C–H bond without fission of the C–C bond to form partial oxidation products from 2-methylpropane. It should be noted that selectivities to propanone and 2-methylpropan-2-ol, which were formed by activation of tertiary C–H bonds, increased and selectivities to COx, 2-methylpropanal and methacrolein decreased in the order Rb > K > Na. The difference of activity and selectivity by the type of alkali ions added to VS may be caused by the following reason. Generally, the base strength of alkali ions is higher with a larger atomic number. It is likely that S 400 interacting with alkali ions possessing the stronger basicity activates tertiary C–H bonds selectively. In addition, alkali ions are anticipated to interact with active sites (VO_4^{3-}) in alkali-ion-modified catalysts [10] and to be adjacent to active sites, from the results of the reaction and photoluminescent spectra [11,12]. Ionic radii of alkali ions are larger with increasing atomic number, and an alkali ion having larger ionic radius has a stronger influence of the electrostatic effect on V=O in VO_4^{3-} which is supposed to be an active site for photooxidation [8,17]. These effects may result in the difference of activity and selectivity in photooxidation among alkali-ion-modified catalysts.

The quantum yield in the photooxidation of 2-methylpropane was evaluated by performing the reaction over Rb-VS by irradiation by light through a monochromator [12]. The amount of photons determined by the method of chemical actinometry was 1.9×10^{-8} mol/s. The quantum yield was estimated as 0.10, assuming that one molecule of 2-methylpropane is converted into products by one photon.

3.2. Effect of added alkali ions

We prepared K^+-modified VS (Kn-VS) from KNO_3 and compared the reactivity of the catalyst (K-VS) prepared from KOH with that from KNO_3. It was reported that VO_4 units were present mainly in basic solutions (pH > 10), $V_2O_7^{4-}$ or $V_3O_9^{3-}$ in solutions of pH 7–10 and the $V_{10}O_{28}$ unit in acidic solutions (pH < 6) [18]. In addition, the active center of VS for photooxidation of alkene and CO was supposed to be surface tetrahedral vanadium oxide, VO_4. It is expected that VO_4 tetrahedra are present as highly dispersed species in the catalysts prepared from KOH, while KNO_3 does not contribute to the high dispersion because the solution is neutral. Table 3 shows the results of the reactions over these catalysts under irradiation by light of wavelengths $\lambda > 310$ nm. Both the K^+-modified catalysts are more active for oxidation of 2-methylpropane than VS. It seems that interaction between K^+ and an active site in VS brings about high activity for photooxidation of light alkanes, regardless of types of added K salts. In addition, the activity of K-VS was higher than that of Kn-VS. It is possible that modification of VS by KOH promotes the formation of active sites, VO_4, for photooxidation, because of its impregnation solution being a strong base, and that the activity of Kn-VS is lower than that of K-VS because the KNO_3 solution, which is neutral, cannot yield highly dispersed vanadium oxide.

Table 2
Photooxidation of 2-methylpropane over VS and alkali-ion-modified VS catalysts by irradiation by light of wavelengths $\lambda > 390$ nm [a]

Catalysts [b]	Conv. [c] (%)	Selectivity [d] (%)							
		IB	PR	AA	AC	TB	BA	ML	COx
VS [e]	5.4	36	8	5	21	0	20	7	0
Na-VS	58.3	18	2	1	39	5	11	5	16
K-VS	77.6	6	1	1	48	16	7	2	15
Rb-VS [e]	82.2	7	1	0	54	22	7	2	1

[a] Catalyst 0.5 g, 2-methylpropane 70 μmol, O_2 140 μmol, irradiation time 60 min.

[b] The contents of alkali-ion are 1, 2, or 4 wt% as Na_2O, K_2O, or Rb_2O, respectively.

[c] Based on introduced 2-methylpropane.

[d] Based on converted 2-methylpropane. IB 2-methylpropene, PR propene, AA ethanal, AC propanone, TB 2-methylpropan-2-ol, BA 2-methylpropanal, ML methacrolein, COx CO and CO_2. Trace amounts of methanol, ethene, propene oxide, propanal, propan-2-ol, and 2-methylpropanol were formed.

[e] Taken from ref. [13].

Table 3
Photooxidation of 2-methylpropane over V_2O_5/SiO_2 modified by KOH or KNO_3 by irradiation by light of wavelengths $\lambda > 310$ nm [a]

Catalyst [b]	Conv. [c] (%)	Selectivity [d] (%)						
		IB	PR	AA	AC	TB	BA	COx
VS	33.4	16	12	10	37	0	16	6
K-VS	72.2	9	1	1	50	8	4	23
Kn-VS	53.1	13	1	1	54	8	8	9

[a] Catalyst 0.5 g, 2-methylpropane 70 μmol, O_2 140 μmol, irradiation time 15 min.

[b] The contents of alkali ion are 2 wt% as K_2O.

[c] Based on introduced 2-methylpropane.

[d] Based on converted 2-methylpropane. IB 2-methylpropene, PR propene, AA ethanal, AC propanone, TB 2-methylpropan-2-ol, BA 2-methylpropanal, COx CO and CO_2. Trace amounts of methanol, ethene, propene oxide, propanal, propan-2-ol, methacrolein, and 2-methylpropanol were formed.

We carried out the reaction over these catalysts by irradiation by light of wavelengths $\lambda > 390$ nm to evaluate the reactivity of S 400 only in K^+-added catalysts prepared from KOH or KNO_3. In addition, in order to examine whether the formation of S 400 needs the addition of alkali ions or not, we prepared VS impregnated with NH_3 aqueous solution (NH_3-VS), which contains no alkali ions but is a basic solution, and carried out the reaction over this catalyst under the same conditions. Table 4 indicates the results. Over NH_3-VS, the reaction did not take place. S 400 is not present in this catalyst. We conclude that the formation of S 400 needs alkali ions and S 400 is a surface vanadium species which interacts with alkali ions. As for the selectivity of the reaction over K-VS and Kn-VS, little difference could be seen, suggesting that the same active species were formed in both the catalysts. However, the activity of Kn-VS was lower than that of K-VS. This result allowed us to speculate that the number of S 400 in K-VS exceeds that in Kn-VS.

In order to make this clear, we measured the photoluminescence of K-VS and Kn-VS to evaluate the relative amounts of S 400 in both the catalysts from the spectra. Fig. 1 depicts the results of the emission spectra excited at 400 nm at room temperature. Both the spectra have the maximum at the same wavelength. This implies the presence of the same active sites in both the catalysts. However, the intensity of the peak of K-VS is higher than that of Kn-VS. This corresponds directly to the concentration of the active species. The number of the sites in K-VS exceeds that in Kn-VS. The amounts of S 400 in the catalysts possibly cause the difference in activity between K-VS and Kn-VS.

3.3. Addition of various salts

V_2O_5/SiO_2 catalysts were impregnated with aqueous solutions of various salts ($Mg(NO_3)_2$, $Eu(NO_3)_3$, $Pr(NO_3)_3$, or $Ce(NO_3)_3$) to elucidate the factor of S 400 formation. The added cations are basic when being in the state of oxide, as well as alkali ions. The results of photooxidation of propane over these catalysts are summarized in table 5. These reactions were carried out under irradiation by light of wavelengths $\lambda > 310$ nm. The activity of the catalysts, except that modified by KNO_3, was lower than that of V_2O_5/SiO_2 catalyst. In particular, the modification by rare earth metal ions caused a considerable drop in conversion of propane. Difference in selectivity was observed for each catalyst. In addition, the presence of S 400 in each catalyst was

Table 4
Photooxidation of 2-methylpropane over V_2O_5/SiO_2 modified by KOH, KNO_3 or NH_3 by irradiation by light of wavelengths $\lambda > 390$ nm [a]

Catalyst [b]	Conv. [c] (%)	Selectivity [d] (%)						
		IB	PR	AA	AC	TB	BA	COx
VS	1.7	42	6	0	23	0	18	tr [e]
NH_3-VS	2.4	31	8	3	28	1	18	tr [e]
K-VS	38.4	10	1	tr [e]	51	13	12	3
Kn-VS	19.9	13	1	tr [e]	52	7	13	3

[a] Catalyst 0.5 g, 2-methylpropane 70 μmol, O_2 140 μmol, irradiation time 15 min.

[b] The contents of alkali-ion are 2 wt% as K_2O.

[c] Based on introduced 2-methylpropane.

[d] Based on converted 2-methylpropane. IB 2-methylpropene, PR propene, AA ethanal, AC propanone, TB 2-methylpropan-2-ol, BA 2-methylpropanal, COx CO and CO_2. Trace amounts of methanol, ethene, propene oxide, propanal, propan-2-ol, methacrolein and 2-methylpropanol were formed.

[e] tr trace amount.

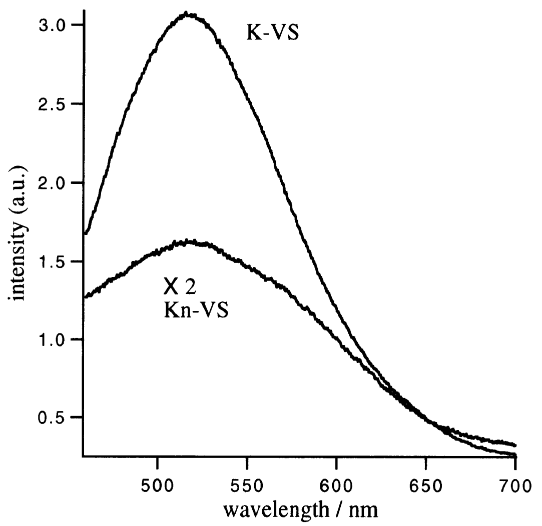

Fig. 1. Photoluminescent emission spectra of K-VS and Kn-VS excited at 400 nm at room temperature. X2 stands for twice amplification in recording.

examined by the reaction by irradiation by light of wavelengths $\lambda > 390$ nm. The results are shown in table 6. The catalyst modified by KNO_3 possesses the highest activity among all the catalysts whereas the others were almost inactive in photooxidation. Difference of activity and selectivity in the reaction over each catalyst may be caused by the interaction between added ion and active site in the catalyst, and/or the formation of vanadate different from that in V_2O_5/SiO_2 catalyst by addition of each salt. As mentioned above, the formation of S 400 is supposed to need alkali ions.

3.4. *Formation of 2-methylpropan-2-ol*

Over alkali-ion-modified VS catalysts, the formation of 2-methylpropan-2-ol was confirmed. It is a very rare case and interesting that 2-methylpropan-2-ol was formed from 2-methylpropane and gaseous oxygen in heterogeneous catalysis. Teichner et al. reported that ketones and aldehydes were formed via intermediates such as alkene and alcohol in the photooxidation of light alkanes over TiO_2 [19]. This conclusion was not drawn from the spectroscopic data, but was deduced from the analysis of the products distribution. We have already proposed the mechanism of the formation of 2-methylpropan-2-ol and propanone in the reaction of 2-methylpropane over Rb^+-modified VS to be as follows [13]:

$$(CH_3)_3CH + V{=}O_L + O_2 \rightarrow (CH_3)_2C{=}O_L + V{=}O + CH_3OH \qquad (1)$$

$$CH_3OH + O_2 \rightarrow HCHO + H_2O + O^* \qquad (2)$$

$$(CH_3)_3CH + O^* \rightarrow (CH_3)_3COH \qquad (3)$$

This mechanism is drawn from the results of the photooxidation of 2-methylpropane by $^{18}O_2$ and time course of the reaction.

We supposed that monoatomic oxygen species (O^*) were formed from the reaction between gaseous oxygen and sacrificial reagent such as methanol. Because only a trace amount of methanol was obtained in the reactions, the precursor to methanol and methanal would be converted to carbon oxides over the catalyst. If 2-methylpropan-2-ol is formed via this mechanism, it is expected that selectivity to 2-methylpropan-2-ol increases by addition of methanol into the reaction system during the photooxidation of 2-methylpropane. To elucidate this, methanol, oxygen and 2-methylpropane were circulated in the reactor and the catalyst bed was irradiated. The result is given in table 7. By adding methanol into the reaction apparatus, selectivity to 2-methylpropan-2-ol increased remarkably. This result substantiates our speculation. In the mechanism of the formation of 2-methylpropan-2-ol, the formation of active oxygen species (O^*) requires a sacrificial reagent such as methanol, and O^* oxidized 2-methylpropane to 2-methylpropan-2-

Table 5
Photooxidation of propane over V_2O_5/SiO_2 modified by various ions by irradiation by light of wavelengths $\lambda > 310$ nm [a]

Added salt [b]	Conv. [c] (%)	Selectivity [d] (%)						
		PR	ET	AA	PA	AC	MeOH	COx
none	35.7	18	4	30	21	22	1	3
KNO_3	54.8	3	1	4	2	55	4	30
$Mg(NO_3)_2$	28.4	9	2	21	8	22	14	22
$Eu(NO_3)_3$	10.3	19	4	7	3	37	8	23
$Pr(NO_3)_3$	5.0	25	5	7	3	49	11	tr [e]
$Ce(NO_3)_3$	3.6	27	9	11	3	13	2	36

[a] Catalyst 0.5 g, propane 70 μmol, O_2 140 μmol, irradiation time 30 min.
[b] The contents of K^+ are 2 wt% as K_2O. The mole ratios (Y/V) are 1.5. (Y = Mg, Eu, Pr, and Ce.)
[c] Based on introduced propane.
[d] Based on converted propane. PR propene, ET ethene, AA ethanal, PA propanal, AC propanone, MeOH methanol, COx CO and CO_2. Trace amounts of propene oxide, and propan-2-ol were formed.
[e] tr trace amount.

Table 6
Photooxidation of propane over V_2O_5/SiO_2 modified by various ions by irradiation by light of wavelengths $\lambda > 390$ nm [a]

Added salt [b]	Conv. [c] (%)	Selectivity [d] (%)						
		PR	ET	AA	PA	AC	MeOH	COx
none	2.6	47	2	14	20	15	0	0
KNO_3	17.2	3	tr [e]	5	8	74	3	6
$Mg(NO_3)_2$	0.7	78	0	0	0	22	0	0
$Eu(NO_3)_3$	0.7	82	0	14	0	4	0	0
$Pr(NO_3)_3$	0.0	–	–	–	–	–	–	–
$Ce(NO_3)_3$	0.1	100	0	0	0	0	0	0

[a] Catalyst 0.5 g, propane 70 μmol, O_2 140 μmol, irradiation time 30 min.

[b] The contents of K^+ are 2 wt% as K_2O. The mole ratios (Y/V) are 1.5 (Y = Mg, Eu, Pr, and Ce).

[c] Based on introduced propane.

[d] Based on converted propane. PR propene, ET ethene, AA ethanal, PA propanal, AC propanone, MeOH methanol, COx CO and CO_2. Trace amounts of propene oxide, and propan-2-ol were formed.

[e] tr trace amount.

ol easily. We have found that selectivity to 2-methylpropan-2-ol increased with irradiation time [13]. At the initial stage of the reaction, the formation of the species working as sacrificial reagents such as methanol described in eq. (1) would be limited and the oxidation to alkenes and ketones would preferentially take place. As the reaction proceeds, the amounts of sacrificial reagents increase to cause the formation of monoatomic oxygen species.

Photooxidation of 2-methylpropane over Rb-VS was carried out in the presence of CO_2 and/or H_2O to investigate the influence of CO_2 and/or H_2O formed in the photooxidation of 2-methylpropane. The result can be found in entry 3 of table 7. Addition of CO_2 and H_2O into the reactor brought about a slight increase in selectivity to 2-methylpropan-2-ol, compared with the result in entry 1. CO_2 and H_2O facilitate the formation of 2-methylpropan-2-ol. This effect was investigated further in detail. Table 8 shows the results. In the absence of gaseous O_2, the conversion level was very low and 2-methylpropene was formed mainly (entry 1). The reaction would not be catalytic. This suggests that the formation of oxygenated products needs gaseous oxygen. On the other hand, selectivity to 2-methylpropan-2-ol increased by adding H_2O and/or CO_2. In the presence of H_2O (entry 2), although conversion of 2-methylpropane was almost of the same level as that in entry 1, the selectivity to 2-methylpropan-2-ol was much higher than that in entry 1. In the presence of CO_2 (entry 3), conversion became higher and the selectivity to 2-methylpropan-2-ol increased slightly in comparison with the result in entry 1. In addition, in the presence of H_2O and CO_2 (entry 4), the conversion was almost of the same level as that in entry 3, and the selectivity to 2-methylpropan-2-ol was the highest among all the reactions under various conditions. The formation of 2-methylpropan-2-ol was possibly promoted by the presence of H_2O and/or CO_2.

In order to elucidate this effect of CO_2 and H_2O, we carried out the photo-assisted reaction of 2-methylpropane with $C^{18}O_2$ and $H_2{}^{18}O$ and examined the content of ^{18}O in the produced 2-methylpropan-2-ol. Fig. 2 shows the time course of conversion and ^{18}O contents in 2-methylpropan-2-ol formed in the photo-assisted reaction of 2-methylpropane. Conversion of 2-methylpropane increased with irradiation time in all the runs. ^{18}O-content in 2-methylpropan-2-ol was low at the initial stage in all the runs, and increased or was kept at almost the same level with irradiation time. Formation of

Table 7
Photooxidation of 2-methylpropane over Rb^+-modified VS catalyst by irradiation by light of wavelengths $\lambda > 390$ nm [a]

Entry	Additive [b]	Conv. [c] (%)	Time [d] (min)	Selectivity [e] (%)					
				IB	PR	AC	TB	BA	ML
1	none	35.2	11	13	2	52	15	12	2
2	MeOH [f]	31.8	15	14	1	41	25	12	2
3	$CO_2 + H_2O$	35.0	15	13	2	53	18	8	2

[a] Catalyst 0.5 g, 2-methylpropane 70 μmol, O_2 140 μmol.

[b] MeOH 36 μmol, CO_2 100 μmol, H_2O 50 μmol.

[c] Based on introduced 2-methylpropane.

[d] Irradiation time.

[e] Based on converted 2-methylpropane. IB 2-methylpropene, PR propene, AC propanone, TB 2-methylpropan-2-ol, BA 2-methylpropanal, ML methacrolein. Trace amounts of ethene, propene oxide, propanal, propan-2-ol, 2-methylpropanol, CO and CO_2 were formed.

[f] MeOH methanol.

Table 8
Photooxidation of 2-methylpropane over Rb-VS in the absence of gaseous oxygen by irradiation by light of wavelengths $\lambda > 390$ nm [a]

Entry	Additive [b]	Conv. [c] (%)	Selectivity [d] (%)		
			IB	AC	TB
1	none	6.6	97	1	2
2	H_2O	6.1	67	2	29
3	CO_2	11.1	86	1	7
4	$H_2O + CO_2$	10.9	59	2	36

[a] Rb-VS 0.5 g, 2-methylpropane 70 μmol, irradiation time 30 min.

[b] H_2O 50 μmol, CO_2 200 μmol.

[c] Based on introduced 2-methylpropane.

[d] Based on converted 2-methylpropane. IB 2-methylpropene, AC propanone, and TB 2-methylpropan-2-ol. Trace amounts of ethenal, propan-2-ol, and 2-methylpropanal were formed.

$C^{16}O^{18}O$ and $C^{16}O_2$ was detected in the reaction in the presence of $C^{18}O_2$. $C^{16}O^{18}O$ and $C^{16}O_2$ were formed by the exchange reaction between $C^{18}O_2$ and lattice oxygen in the catalyst. In addition, this exchange reaction was promoted by the presence of H_2O. These results indicate that lattice oxygen is incorporated into 2-methylpropane at first to form 2-methylpropan-2-ol. The exchange reaction in the presence of $C^{18}O_2$ may result in the increase in ^{18}O content in 2-methylpropan-2-ol with irradiation time. ^{18}O-content in 2-methylpropan-2-ol in the reaction in the presence of H_2O and CO_2 would be the highest among all the runs, because H_2O promoted the exchange reaction between CO_2 and lattice oxygen in the catalyst. Little oxygenated product was formed in the absence of gaseous oxygen and 2-methylpropan-2-ol was formed in the presence of H_2O and CO_2. CO_2 and H_2O may loosen the bond between lattice oxygen and vanadium in the active species for the formation of 2-methylpropan-2-ol. In the photooxidation of 2-methylpropane by $^{18}O_2$ over Rb-VS, ca. 80% of 2-methylpropan-2-ol contained ^{18}O,

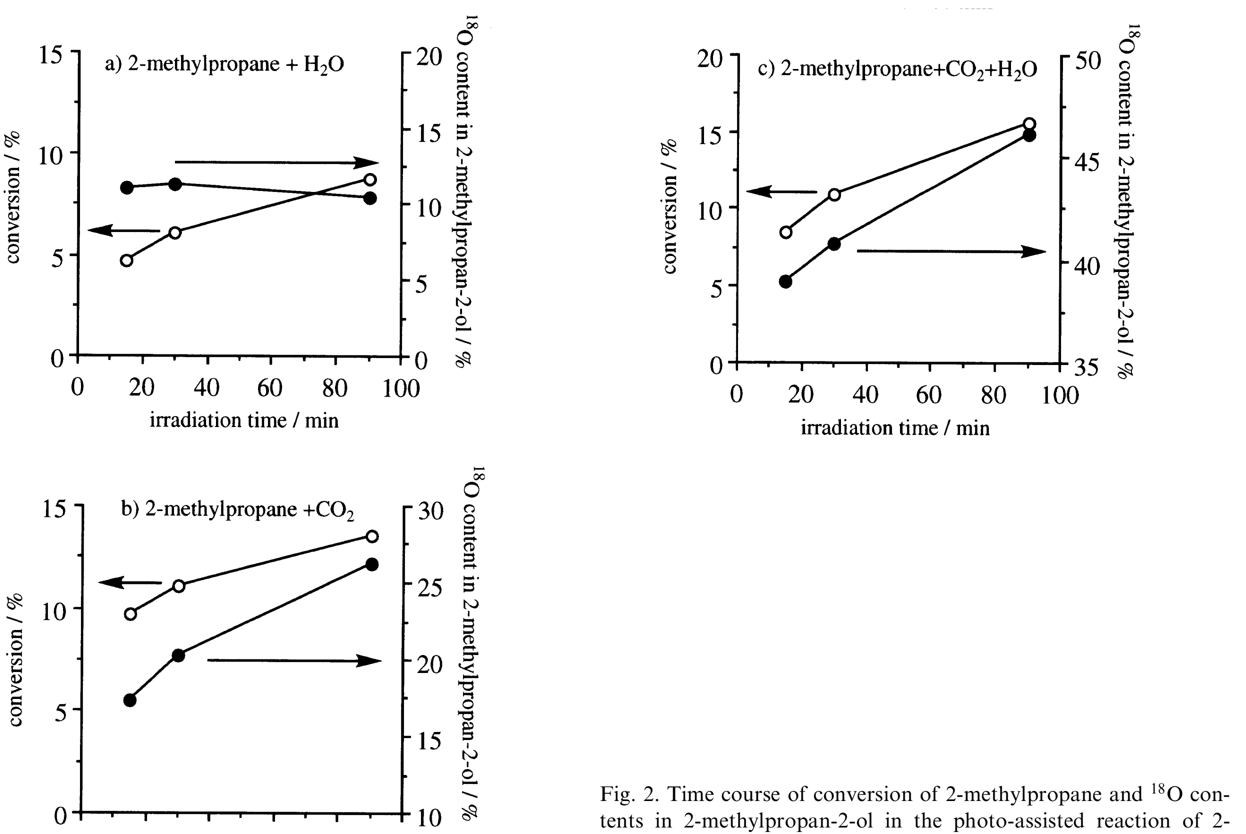

Fig. 2. Time course of conversion of 2-methylpropane and ^{18}O contents in 2-methylpropan-2-ol in the photo-assisted reaction of 2-methylpropane over Rb-VS in the presence of $C^{18}O_2$ and/or $H_2{}^{18}O$ by irradiation by light of wavelengths $\lambda > 390$ nm. Catalyst 0.5 g, 2-methylpropane 70 μmol, $H_2{}^{18}O$ 50 μmol, $C^{18}O_2$ 200 μmol.

and the rest ^{16}O [13]. The ^{18}O content of 2-methylpropane was not much changed during the initial period of the reaction. From these results, we suppose that 2-methylpropan-2-ol was synthesized via two types of reaction paths. One is that O^* formed from gaseous oxygen oxidizes 2-methylpropane to 2-methylpropan-2-ol, shown in eqs. (1)–(3). The other is that lattice oxygen is incorporated into 2-methylpropane. The presence of CO_2 and H_2O facilitates the latter reaction path.

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