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Photo-assisted oxidation of 2-methylpropane over Rb^+ -modified V_2O_5/SiO_2

Formation of 2-methylpropane-2-ol from 2-methylpropane and O₂

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or

The reactivity of the surface species interacting with Rb ions in the photo-oxidation of 2-methylpropane at room temperature has been investigated to clarify the mechanism of photo-oxidation of alkanes. (Propane is oxidized into oxygenates over photo-irradiated V_2O_5/SiO_2 . The addition of alkali metal ions to V_2O_5/SiO_2 greatly enhances the catalytic activity as well as the selectivity to propanone. This is due to the formation of new kinds of surface-active species by interaction between vanadium ions and alkali metal ions. The interaction affects the exciting wavelength of vanadate effective for the oxidation, $\lambda > 400$ nm.) The activity of the species is considerably high. Propanone and C₄-compounds were formed. The most striking point is the formation of 2-methylpropan-2-ol over the Rb⁺-modified catalyst. The reaction path of the formation of 2-methylpropan-2-ol has been studied by analysing the products of the reactions with various sole reactants. The results suggest that the formation of 2-methylpropan-2-ol is not formed *via* 2-methylpropene. A tracer study with ¹⁸O₂ showed that oxygen atoms incorporated into 2-methylpropan-2-ol were from gaseous oxygen, whereas propanone contained ¹⁶O which originated from the lattice oxygen in the catalyst. It is likely that 2-methylpropan-2-ol is formed by mono-oxygenation as found in the enzyme system from 2-methylpropane and gaseous oxygen.

In the photo-assisted oxidations of alkanes over semiconductor photocatalysts, mainly on TiO_2 , alcohol was assumed to be a primary intermediate by Teichner and others,¹ although the formation of alcohols was not evidenced. As an active oxygen species, they proposed monoatomic oxygen with a neutral charge, as found in the case where vacuum UV-irradiated oxygen results in the dissociation of O_2 molecules to cause O* (2D) formation. This monoatomic oxygen easily oxidizes an alkane to an alcohol.²

$$\mathbf{RH} + \mathbf{O}^* \to \mathbf{ROH} \tag{1}$$

where R is an alkyl group. Teichner *et al.* assumed that the formation of such monoatomic oxygen is caused by the reaction between a positive hole p^+ and ionosorbed oxygen species, as follows;^{3,4}

$$O^- + p^+ \to O^* \tag{2}$$

$$O^{2^-} + 2p^+ \to O^* \tag{3}$$

They proposed that this oxygen atom reacts with an alkane to form an alcohol but the alcohol formed is immediately converted to alkenes and/or aldehydes and ketones.

Recently, we have found that atomically-dispersed vanadium oxide on silica (V_2O_5/SiO_2) can catalyse the photoassisted oxidation of propane under irradiation with light of wavelength 310-370 nm, although the oxidation is not selective.⁵ We have also reported that the modification of V_2O_5/SiO_2 with alkali metal ions brought about a great change in the catalytic performance.⁵ Propane is oxidized to propanone selectively over alkali metal ion-modified V_2O_5/SiO_2 irradiated by light with wavelengths longer than 390 nm. On alkali metal ion-modified V_2O_5/SiO_2 , we have found that two active surface vanadates are present.⁶ One is VO_4 (S-310), the same species as present on V_2O_5/SiO_2 ⁷ and the other is vanadate interacting with the alkali metal ions (S- 400). The latter can catalyse the selective oxidation of propane by irradiation with light of wavelengths $\lambda > 390$ nm.

On TiO₂, the total oxidation of alkanes mainly occurs. On the other hand, our photocatalyst is selective but it is likely that the reaction process of the alkane is similar to that on TiO_2 .

In the present paper, we report the photo-assisted oxidation of 2-methylpropane (iso-butane) over irradiated Rb^+ -ionmodified V_2O_5/SiO_2 and discuss the reaction route containing formation of 2-methylpropan-2-ol (*tert*-butanol).

Experimental

 V_2O_5 (2.5 wt.% as V_2O_5)/SiO₂ (VS) was prepared by impregnating SiO₂ with an aqueous solution of ammonium metavanadate, as described elsewhere.⁸ Rb⁺-ion-modified V_2O_5 /SiO₂ (Rb-VS) was prepared by impregnating VS with an aqueous solution of RbOH containing the desired amounts of Rb⁺, followed by calcination in a dry air stream at 773 K for 5 h. The contents of Rb⁺ were 4 wt.% as Rb₂O. No formation of rubidium vanadate compounds on the surface, such as RbVO₃, Rb₃VO₄ or Rb₄V₂O₇, was confirmed by UV–VIS diffuse reflectance spectroscopy. TiO₂ (Degussa P-25) was used after calcination at 773 K in a dried air stream for 5 h.

Prior to each reaction, the catalyst sample was evacuated at 673 K for 1 h and then treated with 6.7 kPa O_2 at 673 K for 2h, followed by evacuation at 673 K for 10 min. The reactions were carried out in a conventional closed circulating system with a quartz reactor.⁹ Photoirradiation was performed at room temperature from a 250 W ultra-high pressure Hg lamp through glass filters, UV-31 or UV-39, passing light with wavelengths of $\lambda > 310$ nm or $\lambda > 390$ nm, respectively. The products were analysed by GLC with three different columns (PEG20M and CBP-10 for the analysis of oxygen-containing products and Shinacarbon for alkanes and alkenes). Every reaction was repeated at least twice to confirm the reproducibility of the data. No reaction proceeded without irradiation of the catalyst samples. Silica, Rb₂O/SiO₂, RbVO₃,

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Table 1 Photo-oxidation of 2-methylpropane over V_2O_5/SiO_2 , $Rb_2O-V_2O_5/SiO_2$ and TiO_2 under irradiation of the light with wavelengths $\lambda > 310 \text{ nm}^4$

		selectivity (%) ^{d,e}							
catalyst ^b	(%)	IB	PR	AA	AC	ТВ	МР	ML	CO _x
V_2O_5/SiO_2 Rb ₂ O-V ₂ O ₅ /SiO ₂	58.4 94.3	8 6	6 1	10 1	36 51	0 5	9 3	1 1	29 31
TiÔ ₂	41.5	1	tr. ^f	tr. ^f	24	0	0	0	74

^{*a*} 2-methylpropane 70 µmol, O₂ 150 µmol, irradiation time 1 h, reaction temperature 308 K. ^{*b*} V₂O₅/SiO₂, Rb₂O-V₂O₅/SiO₂ 500 mg, TiO₂ 200 mg, ^{*c*} Based on 2-methylpropane. ^{*d*} Based on converted 2-methylpropane. ^{*e*} IB: 2-methylpropene (CH₃)₂C=CH₂; PR: propene CH₃CH=CH₂; AA: ethanal CH₃CHO; AC: propanone CH₃COCH₃; TB: 2-methylpropan-2-ol (CH₃)₃COH; MP: 2-methylpropanal (CH₃)₂CHCHO; ML: metacrolein CH₂=C(CH₃)CHO; CO_x: carbon monoxide and carbon dioxide. The other product was a trace amount of methanol. ^{*f*} tr., trace amount.

 Rb_3VO_4 and $Rb_4V_2O_7$ were inactive for the photo-assisted reaction.

Results and Discussion

Photo-assisted oxidation of 2-methylpropane

Table 1 shows the results of the photo-assisted oxidation of 2-methylpropane over VS and Rb-VS catalyst, together with that over TiO₂ as a reference. Photoirradiation was performed with a UV-31 glass filter, which activates both S-310 and S-400 species on Rb-VS. The activity of Rb-VS was the highest of the three. The main products were propanone and carbon oxides in each case. VS was not selective for propanone formation, while in the case of Rb-VS and TiO₂, propanone is selectively formed. However, total oxidation over TiO₂ to form carbon oxides is overwhelming. Despite the highest conversion being on Rb-VS, selectivity to carbon oxides is maintained, although at a lower level. The most striking point for the Rb-VS case is the formation of 2-methylpropan-2-ol. This supports our earlier findings that the addition of alkali metal ions to VS suppresses C—C bond fission in the photo-assisted oxidation of propane.^{5,6}

To examine the catalytic performance by S-400, we carried out the reactions on VS and Rb-VS irradiated through a UV-39 filter, together with TiO₂ as a reference. The results are summarized in Table 2. Under these conditions, the activity of TiO₂ decreased because the 250 W Hg lamp we used has no lines in the region 380-400 nm. The selectivity to CO. decreased and that to 2-methylpropene increased. This is due to low conversion. VS exhibited poor activity, as expected. However, in comparison with the results shown in Table 1, the selectivity to total oxidation decreased significantly and the selectivity of 2-methylpropene increased. The suppression of the formation of carbon oxides is general in oxidation at such a low conversion, as found in the case of TiO_2 . On the other hand, the activity of Rb-VS remained high, indicating that S-400 can be activated by visible light. Despite high conversion, the selectivity to total oxidation was quite low and surprisingly, a fairly large amount of 2-methylpropan-2-ol was produced. Since the selectivity to propanone is almost the same as that shown in Table 1, the route to total oxidation

changed to that of the formation of 2-methylpropan-2-ol. In contrast to the case of VS, the formation of carbon oxides over Rb-VS is not affected by the amount of conversion. The excitation mechanism of the active species would therefore be different for irradiation.

Reaction of 2-methylpropane over photo-irradiated catalysts in the absence of oxygen

In the photo-oxidation of alkenes over VS, lattice oxygen plays an important role.¹⁰ It is likely that lattice oxygen participates directly in the oxidation. To elucidate this, only 2methylpropane was circulated in the reaction apparatus and the catalyst bed was irradiated. After 1 h irradiation, the gas was analysed. The results are shown in Table 3. The conversion was suppressed to a low level in each case. In all cases, the main product was 2-methylpropene. However, the same amount of propanone was found over VS. This strongly suggests that activated lattice oxygen was incorporated directly in the reaction for the case of VS, as found in the photooxidation of olefins.^{10,11} On the other hand, only a small amount of propanone was formed on Rb-VS, independent of the type of UV filter used for irradiation. If Rb-VS contained comparable amounts of both S-310 and S-400, more appreciable amounts of propanone would have been obtained when irradiation was carried out through a UV-31 filter. This suggests that most of the vanadates on the surface are S-400 affected by rubidium ions. Therefore, S-400 is also excited by light with wavelengths 310-390 nm. 2-Methylpropene was formed with a high selectivity, indicating that, over Rb-VS oxidative dehydrogenation of 2-methylpropane proceeded preferentially.

Time evolution of photo-assisted oxidation of 2-methylpropane

Fig. 1 shows the time evolution of the conversion and yields of products in the photo-assisted oxidation of 2-methylpropane over Rb-VS irradiated through a UV-39 filter. Almost no production of carbon oxides was observed. In the first ten minutes, the conversion increases proportionally with irradiation time, and then the rate slows. The yields of propanone and 2-methylpropan-2-ol varied in a similar manner with irradiation time. However, the yields of 2-methylpropene, 2-

Table 2 Photo-oxidation of 2-methylpropane over V_2O_5/SiO_2 and $Rb_2O-V_2O_5/SiO_2$ under irradiation of the light with wavelengths $\lambda > 390$ nm^a

-		selectivity (%) ^{c,d}							
catalyst	(%)	IB	PR	AA	AC	ТВ	МР	ML	CO _x
V ₂ O ₅ /SiO ₂	5.4	36	8	5	21	0	20	7	2
Rb ₂ O-V ₂ O ₅ /SiO ₂	82.2	7	1	0	54	22	7	2	1
TiO ₂	11.3	26	4	1	14	0	tr. ^e	tr."	54

^a 2-methylpropane 70 μ mol, O₂ 150 μ mol, irradiation time 1 h, reaction temperature 308 K, catalyst 500 mg, except TiO₂ (200 mg). ^b Based on 2-methylpropane. ^c Based on converted 2-methylpropane. ^d IB, PR, AA, AC, TB, MP, ML and CO_x, see footnote of Table 1.^e tr., trace amount.

Table 3 Photo-assisted reaction of 2-methylpropane over V₂O₅/SiO₂ and Rb₂O-V₂O₅/SiO₂ under irradiation^a

	I IX/b					selectiv	vity (%) ^{d,e}			
catalyst	irradiation	(%)	IB	PR	AA	AC	ТВ	МР	ML	COx
V ₂ O ₅ /SiO ₂	UV31	9.0	75	4	0	15	0	0	0	0
$Rb_2O-V_2O_5/SiO_2$	UV31	15.2	88	1	0	3	3	0	0	0
$Rb_2O-V_2O_5/SiO_2$	UV39	9.1	92	tr.	0	3	1	1	tr. ^f	0

^a 2-methylpropane 70 μ mol, irradiation time 1 h, reaction temperature 308 K, catalyst 500 mg. ^b UV31 and UV39 are the filters for irradiation, see text. ^c Based on 2-methylpropane. ^d Based on converted 2-methylpropane. ^e IB, PR, AA, AC, TB, MP, ML and CO_x, see footnote of Table 1. ^f tr. trace amount.

methylpropanal and methacrylaldehyde (metacrolein) reached a constant value after 10 min. Since it is unlikely that propanone and 2-methylpropan-2-ol are formed via metacrolein and 2-methylpropanal, the latter two are thought to be final products. In order to obtain information about the reaction path, we plotted the selectivities for these partial oxidation products against irradiation time, as shown in Fig. 2. The selectivity for propanone was almost constant. The selectivities to 2methylpropene, metacrolein and 2-methylpropanal decreased with irradiation time, suggesting that these products were formed through the same reaction path. On the other hand,



Fig. 1 Time evolution of the conversion and products yield in the photo-oxidation of 2-methylpropane over Rb^+ -ion-modified V_2O_5/SiO_2 . Photoirradiation was carried out through a UV-39 glass filter ($\lambda > 390$ nm) at room temperature. O: conversion based on 2-methylpropane, \times : propanone (CH₃COCH₃), \bigcirc : 2-methylpropan-2-ol [(CH₃)₃COH], \triangle : 2-methylpropanal [(CH₃)₂CHCHO], \square : 2-methylpropene [(CH₃)₂C=CH₂], \blacktriangle : 2-methylprop-3-enal [CH₂=C(CH₃)CHO]. CO_x yield was less than 1% and a trace amount of methanol was detected.

the selectivity to 2-methylpropan-2-ol increased with irradiation time. This might suggest that 2-methylpropan-2-ol is a secondary product. It may be formed by hydration of 2methylpropene with water molecules which arise during oxidation.

Photo-assisted oxidation of 2-methylpropene and 2-methylpropan-2-ol

It is generally accepted that hydration of an alkene proceeds in the presence of acid sites. The participation of acid sites in photo-assisted reactions such as the dehydration of alcohols has been suggested in several reports.¹² However, as found in our earlier work, addition of alkali metal ions brought about the elimination of acid sites.¹³ Therefore, the hydration of 2methylpropene on acid sites in the present system is hardly an acceptable notion. To clarify these processes, we have carried out the photo-assisted oxidation of 2-methylpropene over



Fig. 2 Time course of the products selectivity in the photo-oxidation of 2-methylpropane over Rb^+ -ion-modified V_2O_5/SiO_2 . Captions as in Fig. 1.

Table 4 Photo-assisted oxidation of 2-methylpropene over Rb₂O-V₂O₅/SiO₂ under irradiation^a

	* 7 * 7h		•	selectivity (%) ^{d.e}						
entry	irradiation	added water /µmol	(%)	PR	AA	AC	ТВ	MP	ML	COx
1	UV31	0.0	56.3	tr.	1	13	0	1	32	51
2	UV31	20.0	54.9	1	1	13	0	1	30	52
3	UV39	0.0	28.1	1	tr.	7	0	2	34	54
4	UV39	20.0	28.0	1	1	6	0	1	33	56

^a 2-methylpropene 70 μ mol, O₂ 150 μ mol, irradiation time 30 min, reaction temperature 308 K, catalyst 500 mg. ^b UV31 and UV39 are the filters for irradiation, see text. ^c Based on 2-methylpropene. ^d Based on converted 2-methylpropene. ^e PR, AA, AC, TB, MP, ML and CO_x, see footnote of Table 1. Other products were trace amounts of ethene, acrolein and propanal.^f tr., trace amount.

Table 5	Photo-assisted oxidation	of 2-methylpropan-2-ol	over Rb ₂ O-V ₂ O ₅ /SiO ₂	under irradiation ^a
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111/0	oppupation (selectivity (%) ^{d.e}			
irradiation	(%)	IB	AC	CO _x	
UV31 UV39	57 5.7	12 59	33 24	55 18	
	UV31 UV39	UV3157UV395.7	UV31 57 12 UV39 5.7 59	UV31 57 12 33 UV39 5.7 59 24	

^a 2-methylpropan-2-ol 18 µmol, O₂ 24 µmol, irradiation time 15 min, reaction temperature 308 K, catalyst 500 mg. ^b UV31 and UV39 are the filters for irradiation, see text. ^c Based on 2-methylpropan-2-ol. ^d Based on converted 2-methylpropan-2-ol. ^e IB, AC and CO_x, see footnote of Table 1.

Rb-VS in the presence and absence of water molecules. The results are summarized in Table 4.

It is evident that product selectivities are quite different from those in the photo-assisted oxidation shown in Tables 1 and 2, indicating that 2-methylpropene is not a main intermediate at all. The main products were CO_x and metacrolein. Formation of propanone was suppressed slightly. Addition of water molecules to the system, indicated as entries 2 and 4, did not change the products selectivities. No 2-methylpropan-2-ol was formed in any runs. Accordingly, we conclude that the 2-methylpropan-2-ol produced in the photo-assisted oxidation of 2-methylpropane over Rb-VS did not arise from the hydration of 2-methylpropene.

Table 4 contains another important result when one considers the reaction mechanism: the conversion of 2methylpropene (28.0%, entry 3) is lower than that of 2-methylpropane (60.2%, depicted in Fig. 1). In oxidation, alkenes are ordinarily more reactive than the corresponding alkanes.¹⁴ In the case of alkene oxidation, it was thought that the alkene is adsorbed in an electron donation process. However, the present result suggests the opposite. Addition of alkali metal ions may increase the electron density of the active sites, causing active vanadates which are more basic than those on VS. In other words, addition of alkali metal ions raises the LUMO (lowest unoccupied molecular orbital) level, resulting in a decrease in the ease of accepting electron(s) from the alkenes.¹⁵ In the present system, the basic character may make abstraction of hydrogen from alkane easier.

For alkane photo-oxidation over irradiated TiO₂, an alcohol molecule is thought to be a transitory intermediate, which is quickly transformed to an alkene by dehydration.¹ This possibility in our system was examined by the reaction of 2-methylpropan-2-ol as a sole reactant. Irradiation of the Rb-VS through UV-31 and UV-39 filters in contact with 2methylpropan-2-ol and oxygen was carried out for 15 min. The results are shown in Table 5. In the case of the irradiation through a UV-31 filter, oxidation to propanone and carbon oxides proceeds very rapidly. No formation of aldehydes was observed. Dehydration to produce 2-methylpropene was a minor path. In the case of irradiation through a UV-39 filter, the conversion of 2-methylpropan-2-ol was low and selectivity to 2-methylpropene was high. The difference of conversion of 2-methylpropan-2-ol with the glass filters used explains the difference in the yield of 2-methylpropan-2-ol in 2methylpropane photo-oxidation given in Tables 1 and 2.

Active oxygen species

In order to find out which oxygen species are incorporated in oxygenated products, we have carried out the photo-assisted oxidation of 2-methylpropane with ${}^{18}O_2$ over Rb-VS and we have measured the ${}^{18}O$ distribution in the propanone and 2-methylpropan-2-ol produced. Table 6 shows the variation of ${}^{18}O$ distribution in the products. The ${}^{18}O$ content in the ketone is low and increases gradually with the irradiation time, while in the alcohol the ${}^{18}O$ content is already very high after the first 2 min irradiation and the value is almost constant throughout the irradiation time. The result indicates that

the lattice oxygen of the surface vanadates is incorporated into propanone, and that the oxygen incorporated into 2methylpropan-2-ol originates from gaseous oxygen molecules. From analogy with the photo-oxidation of olefins over irradiated VS,^{10,11} the formation of propanone can be expressed by:

$$(CH_3)_3CH + V = O + {}^{18}O_2$$

 $\rightarrow (CH_3)_2C = O + V = {}^{18}O + CH_3 {}^{18}OH$ (4)

Adsorbed O_2 would play a role in the abstraction of a methyl group from 2-methylpropane and in the restoration of the lattice oxygen in vanadyl. This explains why the ¹⁸O content increases with time. Since only a trace of methanol was obtained in the reaction and the precursor to methanol would convert to carbon oxides, we did not determine the ¹⁸O concentration in the methanol formed.

However, in the case of 2-methylpropan-2-ol formation, the mechanism is complex. In our $Rb_2O-V_2O_5/SiO_2$ system, no exchange reaction or equilibration reaction of ${}^{18}O{-}^{16}O$ occurs and a positive hole, if present, is thought to be localized on an oxygen atom in V=O. Hence, the notion of the formation of active monoatomic oxygen species described in eqn (2) and (3) is hardly acceptable. If the monoatomic oxygen, were to originate from gaseous oxygen, mono-oxygenation, as found in the enzyme system, would require a sacrificial reagent to form active oxygen species as follows:

$$O_2 + 2H^+ + 2e^- \rightarrow O^* + H_2O$$
 (5)

What we call the sacrificial reagent is hydrogen or protons and electrons, as in eqn (5). The selectivity to 2-methylpropan-2-ol increased with reaction time, as shown in Fig. 2. At the initial stage of the reaction, the species working as sacrificial reagents would be limited and the oxidation leading to the production of alkenes, aldehydes and a ketone would preferentially take place. As the reaction proceeds, the amount of sacrificial reagents such as methanol in eqn (4), increases to cause the formation of monoatomic oxygen species, as indicated in eqn (5). In the model enzyme system, the sacrificial reagents are supplied from acetic acid and zinc metal found in Gif systems.¹⁶ In addition, Funabiki *et al.* reported that hydroquinone acts as the hydrogen donor in eqn. (5).¹⁷

The active oxygen species for mono-oxygenation is presumably the same as those found in the model enzyme system. The present work is partially supported by a Grant-in-Aid on Priority-Area-Research 'Photoreaction Dynamics' from the

Table 6 ^{18}O distribution (%) in oxygenated products in photo-oxidation of 2-methylpropane with $^{18}O_2$ over Rb₂ O–V₂O₅/SiO₂ a

	irradiation time/min					
product	2	5	15			
CH ₃ COCH ₃ (CH ₃) ₃ COH	14 85	18 80	25 82			

 a Catalyst 500 mg, 2-methylpropane 40 $\mu mol,\,^{18}\mathrm{O}_2$ (>99%) 40 $\mu mol.$

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