

Effect of alkali-metal ion addition to silica-supported molybdenum oxide on photocatalysis

Photooxidation of propane and propene, and photo-assisted metathesis of propene

Sakae Takenaka, Tsunehiro Tanaka, Takuzo Funabiki and Satohiro Yoshida*

Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 606-01, Japan

The effect of adding alkali-metal ions (Li^+ , Na^+ , K^+ , and Rb^+) to silica-supported molybdenum oxide ($\text{MoO}_3/\text{SiO}_2$) has been investigated by photooxidation of propane and propene with gaseous oxygen, and photo-assisted metathesis of propene at room temperature. Over alkali-metal ion modified $\text{MoO}_3/\text{SiO}_2$, propanone has been mainly produced from propane, and acrolein from propene, whereas over $\text{MoO}_3/\text{SiO}_2$ a variety of products have been formed, such as ethanal, propene, propanone and propanal from propane, and ethanal and acrolein from propene. The photooxidation selectivities change upon the addition of alkali-metal ions because the electrophilicity of the oxygen atom in the molybdenum species in the excited state (*i.e.*, it is active for photooxidation) is weakened by the interaction with the alkali-metal ions. In the photo-assisted metathesis reaction of propene, the conversion is lower over alkali-metal ion modified $\text{MoO}_3/\text{SiO}_2$ than over $\text{MoO}_3/\text{SiO}_2$. The activity for the metathesis reaction has been related to the reducibility of the surface molybdenum species by CO under UV light irradiation. In addition, the Raman spectra suggest that the surface molybdenum species in alkali-metal ion modified $\text{MoO}_3/\text{SiO}_2$ is like $\text{Mo}_2\text{O}_7^{2-}$ besides a small amount of MoO_4^{2-} , whereas the molybdenum species in $\text{MoO}_3/\text{SiO}_2$ exists as a mononuclear species.

Alkali-metal ions are frequently used as promoters in many catalytic systems to improve the selectivity and the activity, as surface acidity can be considered as one of the main factors controlling the catalytic properties. One distinct function of alkali-metal ions is their electron-donating ability, which leads to an enhancement of basicity of metal oxides, but the exact nature and role of the alkali-metal ions are still not well understood. Alkali-metal ions act as both promoters and poisons, for example, potassium ions are often added to iron-based catalysts for Fischer–Tropsch reactions in order to promote activity,¹ whereas the addition of potassium ions to vanadyl pyrophosphate poisons the selective oxidation of *n*-butane to maleic anhydride.²

Supported molybdenum oxide catalysts are excellent for the selective oxidation of hydrocarbons,³ the oxidative dehydrogenation of alcohols,⁴ and the metathesis reaction of alkenes.⁵ Supported molybdenum oxide catalysts are also modified by alkali-metal ions in order to improve catalytic performance. For example, the modification of bismuth- and molybdenum-containing systems by alkali-metal ion improves selectivity to partial oxidation products in the ammoxidation of alkanes.⁶ For oxidation of methane by N_2O over silica-supported molybdenum oxide catalyst, modification by sodium ion poisons the formation of formaldehyde at low loadings of molybdenum oxides, whereas the formation of formaldehyde is promoted by the addition of sodium ions at fairly high loadings of molybdenum oxides.⁷ Bañares *et al.* reported the effect of the addition of alkali-metal ions to silica-supported molybdenum oxide for oxidation of methanol and methane.⁸ Addition of alkali-metal ions decreases the number of isolated surface molybdenum oxide species and brings about the formation of new alkali-metal–molybdate compounds. The oxygen associated with the alkali-metal–molybdate compounds is generally not available for oxidation reactions and the addition of alkali-metal ions decreases catalytic activity for the oxidation of methane and methanol. As for supported molybdenum oxide, the addition of alkali-metal ions often leads to a decrease in activity for oxidation.

Photocatalysis by supported metal oxides is also influenced by the addition of alkali-metal ions. We have already reported

the effect of alkali-metal ion addition on photocatalysis by silica-supported vanadium oxide ($\text{V}_2\text{O}_5/\text{SiO}_2$).^{9–14} Alkali-metal ion modified $\text{V}_2\text{O}_5/\text{SiO}_2$ selectively catalyses the photooxidation of propane to propanone by gaseous oxygen at room temperature, while a variety of products, such as ethanal, propanal, propanone, are produced from propane over $\text{V}_2\text{O}_5/\text{SiO}_2$.^{9,10} The added alkali-metal ion is found to be located adjacent to the surface vanadium species, VO_4 as determined by spectroscopic methods, such as XAFS and Raman spectroscopy.¹³ We have concluded that the change in photocatalytic performance on addition of alkali-metal ions results from a change in the electronic states of the vanadium species, *i.e.*, the electrophilicity of the oxygen atom in the vanadium species in the triplet state, which is active for the photooxidation, becomes weak upon the interaction with alkali-metal ions.¹⁴ Silica-supported molybdenum oxide ($\text{MoO}_3/\text{SiO}_2$) also exhibits photocatalytic activity under UV light irradiation, and catalyses the oxidation of propane¹⁵ and the metathesis reaction of propene.¹⁶ An investigation into photocatalysis by alkali-ion modified metal oxides would be helpful in order to understand the effect of alkali-metal ion addition, as the photocatalytic performance of the metal oxide is sensitive to the addition of alkali-metal ions, as mentioned above.

In this work, we carried out the oxidation of hydrocarbons (propane and propene) by gaseous oxygen and the metathesis of propene over alkali-metal ion modified $\text{MoO}_3/\text{SiO}_2$ under UV light irradiation, and we investigated the effect of alkali-metal ion addition on photocatalysis.

Experimental

Materials

The reactants (propane, propene and oxygen), tetraethylorthosilicate (TEOS, Nacalai Tesque, EP grade), ammonium heptamolybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$, Nacalai Tesque, GR grade], $\text{LiOH}\cdot\text{H}_2\text{O}$ (Wako Pure Chemical Industries, GR grade), NaOH (Nacalai Tesque, GR grade), KOH (Nacalai Tesque, GR grade), and $\text{RbOH}\cdot\text{H}_2\text{O}$

(Mitsuwa's Pure Chemicals, GR grade) were commercially supplied. The gaseous reactants were refined by vacuum distillation at low temperatures. $^{18}\text{O}_2$ was supplied from Isotec Inc. (purity 98.1%) and was used without further purification.

Preparation of samples

A silica support (BET surface area: $556\text{ m}^2\text{ g}^{-1}$) was prepared by hydrolysis of distilled TEOS and calcination at 773 K for 5 h in a dry air stream as described elsewhere.¹⁷ Silica-supported molybdenum oxide (MS) was prepared by impregnating the silica with an aqueous solution of ammonium heptamolybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$ at 353 K for 2 h and by drying up impregnated sample. The sample was dried at 363 K for 12 h and calcined in a dry air stream at 773 K for 5 h. The amount of molybdenum oxide loaded was 4.0 wt.% as MoO_3 . Alkali-metal ion modified silica-supported molybdenum oxide samples (Li-MS, Na-MS, K-MS, and Rb-MS) were prepared by impregnating MS with aqueous solutions of $\text{LiOH}\cdot\text{H}_2\text{O}$, NaOH , KOH , and $\text{RbOH}\cdot\text{H}_2\text{O}$, respectively, followed by calcination in a dry air stream at 773 K for 5 h, in the same manner as mentioned above. Unless otherwise noted, alkali-metal ions equimolar with the molybdenum atoms in MS were added.

Pretreatment of the samples

MS and alkali-metal ion modified MS samples were pretreated by evacuation at 673 K for 1 h, treatment of gaseous oxygen (60 Torr) at 673 K for 2 h and evacuation at 673 K for 10 min prior to reactions and spectral measurements.

Reactions

The reactions were performed in a conventional closed gas-circulating system (dead space: 280 cm^3) described elsewhere.¹⁷ The powder sample (0.5 g) was spread on the flat bottom of a quartz reactor and irradiated by the light from a 250 W ultrahigh pressure Hg lamp at room temperature. The experiments were repeated more than twice to examine the reproducibility of the data. In the dark, the reactions did not take place. After each run, the catalyst bed was heated to 573 K for the collection of products that tightly adsorbed on the catalyst at room temperature. The desorbed products were frozen out in a trap cooled by liquid nitrogen, and were analysed by GLC and GLC-mass spectrometry.

Raman spectra

The laser Raman spectra were taken with the 514.5 nm line of an argon laser (JASCO NRS-2000). The incident laser power at the sample was 30 mW. Spectra were recorded with a resolution of 4 cm^{-1} .

Results

Photooxidation of propane

Table 1 shows the results of the photooxidation of propane with gaseous oxygen over MS and alkali-metal ion modified

MS at room temperature for 10 min. The photooxidation of propane took place efficiently over all the samples and no significant difference in the activity could be found among the five samples. The activities of the alkali-metal ion modified samples were almost the same, regardless of the type of alkali-metal ion added. In the oxidation over MS, propene, ethanal, propanone, propanal *etc.*, were formed, *i.e.*, the reaction was not selective. However, the selectivity to propanone was higher and the selectivities to propene and ethanal were lower over alkali-metal ion modified MS, compared with those over MS, *i.e.*, the alkali-metal ion modified MS samples are effective at incorporating an oxygen atom into a propane molecule without fission of a C—C bond. The trend is remarkable with the large atomic numbers of the added alkali-metal ions. The change in selectivities on addition of the alkali-metal ions to MS indicates that the alkali-metal ions interact with the active molybdenum species for the photooxidation.

We carried out photooxidation of propane over Na^+ -modified MS samples with different amounts of sodium ions in order to investigate further the interaction of the alkali-metal ions with the surface molybdenum species. The results are shown in Fig. 1. The Na : Mo molar ratio was changed from 0 to 1.7. Although the activities for the photooxidation of propane decreased with an increase in the amounts of sodium ions added, the change in the conversion was not so appreciable as that for the yields of partial oxidation products, in particular, propanone. The yield of each product changed linearly with the molar ratio up to Na : Mo = 1.0, *i.e.*, the yields of propene and ethanal decreased, and those of propanal and propanone increased. These results suggest that the addition of sodium ions up to Na : Mo = 1.0 brings about the formation of the molybdenum species that interacts with the sodium ions, which mainly converts propane to propanone. In contrast, with Na : Mo > 1.0, the yield of each product did not change very much. A sluggish decrease in the conversion

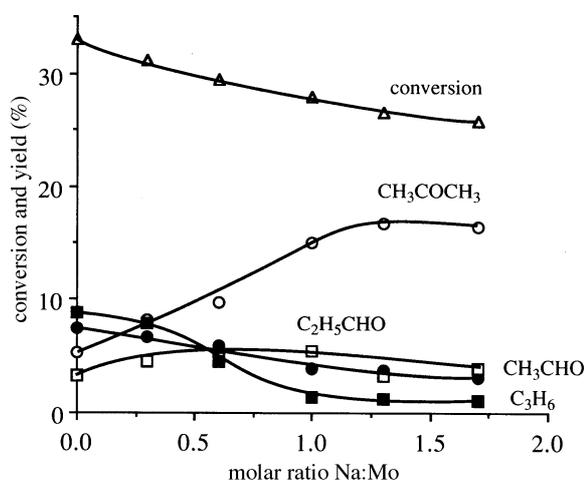


Fig. 1 Change in the conversion and yield of partial oxidation products on photooxidation of propane over Na^+ -modified MS samples with different amounts of sodium ions

Table 1 Photooxidation of propane with gaseous oxygen over MS and alkali-metal ion modified MS at room temperature^a

sample	conv. ^b (%)	selectivity ^c (%)						CO_x
		C_3H_6	CH_3CHO	$\text{C}_2\text{H}_5\text{CHO}$	$(\text{CH}_3)_2\text{CO}$	$\text{C}_2\text{H}_3\text{CHO}$		
MS	33.0	26	22	10	16	1	21	
Li-MS	32.5	15	18	11	23	2	24	
Na-MS	28.0	5	14	19	54	tr ^d	1	
K-MS	25.8	3	7	8	72	1	3	
Rb-MS	35.8	2	5	5	66	1	18	

^a MS and alkali-metal ion modified MS: sample, 0.5 g; propane, 70 μmol ; oxygen, 70 μmol ; and irradiation time, 10 min. ^b Based on introduced propane. ^c Based on converted propane. The other products were trace amounts of ethene, propylene oxide, propan-2-ol, and propan-1-ol. ^d tr = traces.

and yield of propanone was observed on increasing the amounts of sodium ions added. It is likely that the addition of sodium ions to more than the molar ratio Na : Mo = 1 does not bring about the formation of the active species, which mainly produces propanone from propane, but leads to the formation of an alkali-metal–molybdate species, which is inactive for photooxidation. Therefore, the molybdenum species that forms propanone from propane would be a complex comprised of a molybdenum ion and a sodium ion.

Photooxidation of propene

Table 2 shows the results of the photooxidation of propene with gaseous oxygen over MS and alkali-metal ion modified MS. Photoirradiation was carried out at room temperature for 20 min. Conversion of propene over Li-MS and Na-MS was almost the same as that over MS, whereas the conversion over K-MS and Rb-MS was twice that over MS. In the photooxidation of propene over MS, ethanal, acrolein, propanal, ethene, *etc.*, were formed. The addition of alkali-metal ions to MS resulted in an increase in selectivity to acrolein. Over Li-MS and Na-MS, the formation of ethanal and CO_x was depressed and that of acrolein was preferred, compared with those over MS. Over K-MS and Rb-MS, selectivities to ethene, ethanal, propanal, and propanone decreased, and those to acrolein and CO_x increased in comparison with those over MS. Because the conversion levels of propene over K-MS and Rb-MS were higher than those over the other samples, the selectivity to CO_x would be higher over K-MS and Rb-MS. These results indicate that the molybdenum species interacts with some of the alkali-metal ions to convert propene to oxygen-containing products, especially acrolein, without fission of a C–C bond.

We also carried out photooxidation of propene over Rb⁺-modified MS samples with different amounts of rubidium ions. The results were shown in Fig. 2. The conversion of propene and the yield of acrolein became higher with an increase in the amounts of rubidium ions added up to a molar ratio Rb : Mo = 1.0. In the range Rb : Mo = 1.0–2.0, a decrease in conversion and in the yield of acrolein was observed. These results are similar to those for the photooxidation of propane over Na⁺-modified MS with different amounts of sodium ions, suggesting that on addition of rubidium ions up to a molar ratio Rb : Mo = 1.0, the active species

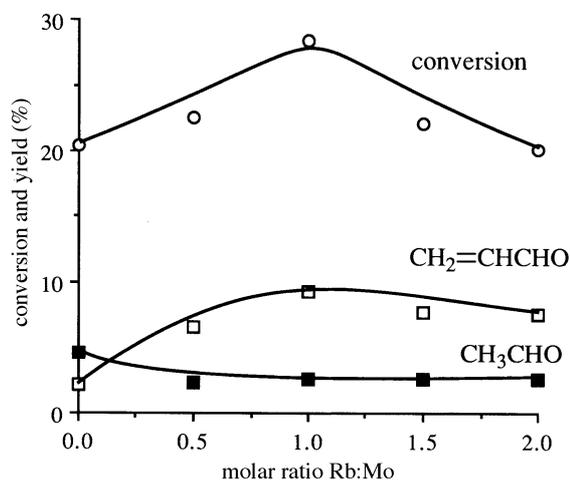


Fig. 2 Change in the conversion and yield of partial oxidation products on photooxidation of propene over Rb⁺-modified MS samples with different amounts of rubidium ions

that convert mainly propene to acrolein are formed, and the addition of rubidium ions to more than Rb : Mo = 1.0 causes the formation of a species inactive for the photooxidation.

Photo-assisted metathesis reaction of propene

We carried out a photo-assisted metathesis reaction of propene over MS and alkali-metal ion modified MS at room temperature in order to investigate further the effect of the addition of alkali-metal ions to MS. The results are found in Table 3. Although the metathesis reaction took place over all the samples under UV light irradiation, the activity became less on the addition of alkali-metal ions to MS and the decrease in the activity became more noticeable with the larger atomic numbers of the added alkali-metal ions. It has been reported that prerduction of MoO₃/SiO₂ by hydrogen, carbon monoxide, or propene, which are known to produce molybdenum ions in a low oxidation state, results in an increase in activity of the metathesis reaction,^{18,19} whereas unreduced MoO₃/SiO₂ is a poor catalyst for the reactions.^{20,21} This suggests that the active species for the metathesis reaction over supported molybdenum oxide catalysts is the surface molybdenum oxide in a low oxidation state.

Table 2 Photooxidation of propene with gaseous oxygen over MS and alkali-metal ion modified MS at room temperature^a

sample	conv. ^b (%)	selectivity ^c (%)					
		C ₂ H ₄	CH ₃ CHO	C ₂ H ₅ CHO	(CH ₃) ₂ CO	C ₂ H ₃ CHO	CO _x
MS	11.6	12	32	12	6	24	13
Li-MS	12.1	21	27	10	6	30	tr ^d
Na-MS	13.2	14	21	10	4	48	tr ^d
K-MS	22.5	6	11	5	2	41	35
Rb-MS	21.1	4	9	5	1	39	40

^a MS and alkali-ion-modified MS: sample 0.5 g; propene, 70 μmol; O₂, 70 μmol; and irradiation time, 20 min. ^b Based on introduced propene.

^c Based on converted propene. The other product was trace amounts of propylene oxide. ^d tr = traces.

Table 3 Photo-assisted metathesis of propene over MS and alkali-metal ion modified MS at room temperature^a

sample	conv. ^b (%)	product distribution ^c /mol%			
		C ₂ H ₄	1-C ₄ H ₈	<i>trans</i> -2-C ₄ H ₈	<i>cis</i> -2-C ₄ H ₈
MS	42.7	63	8	19	8
Li-MS	40.7	61	7	19	8
Na-MS	33.3	58	51	25	11
K-MS	14.5	55	3	23	12
Rb-MS	5.5	57	3	24	14

^a MS and alkali-metal ion modified MS: sample, 0.5 g; propene, 70 μmol, and irradiation time, 20 min. ^b Based on introduced propene. ^c The other products were trace amounts of hexenes, ethanal, propylene oxide, propanone and propanal.

Martin *et al.*²² and O'Young²³ have also reported that the reducibility of the molybdenum species on the supports is decreased by the addition of alkali-metal ions. Hence, we expected that the activity for photo-assisted metathesis would decrease on addition of alkali-metal ions because the surface molybdenum oxide that interacts with the alkali-metal ions is difficult to reduce under UV irradiation. In order to confirm whether or not our speculation was reasonable, we carried out photoreduction of the molybdenum species in MS and alkali-metal ion modified MS by gaseous CO at room temperature, and investigated the amount of carbon dioxide formed. The photoreduction of MS and alkali-metal ion modified MS by CO gas was carried out in the closed gas-circulating system with the trap cooled by liquid nitrogen in a circulating path. The CO₂ formed by photoreduction of the molybdenum species was trapped immediately, hence we could monitor the change in pressure of the gaseous CO. Fig. 3 shows the results. Over all the samples a decrease in the pressure of CO was observed under UV light irradiation, suggesting that all the samples were reduced. The rate of decrease in the pressure of CO over MS was the fastest of all the samples, and the rate became slower the larger the atomic number of the alkali-metal ion added, *i.e.*, Li > Na > K > Rb. In addition, the largest total amount of CO₂ formed was in the photoreduction over MS, and the amount decreased for the alkali-metal ion modified MS in the order Li-MS > Na-MS > K-MS > Rb-MS. These results suggest that the molybdenum species in alkali-metal ion modified MS are more difficult to reduce than those in MS; the interaction of the alkali-metal ion with the surface molybdenum species would cause this effect. The reducibility of the molybdenum species by CO under UV light irradiation is compatible with the activity for the photo-assisted metathesis of propene. Therefore, the reducibility of the surface molybdenum species under UV light irradiation would be one of the factors determining the activity for photo-assisted metathesis of propene.

Raman spectra

The Raman spectra gave helpful information about the active species on a silica support. Fig. 4 shows the Raman spectra of MS and Na-MS. A band was found at 986 cm⁻¹ in the Raman spectrum of MS. The band at 986 cm⁻¹ was assigned to terminal Mo=O stretching vibration of an isolated molybdenum species on the silica support.²⁴ Five sharp bands at 936, 918, 888, 870, and 830 cm⁻¹ were observed in the Raman spectrum of Na-MS, indicating that the alkali-metal-molybdate species were formed by the addition of sodium

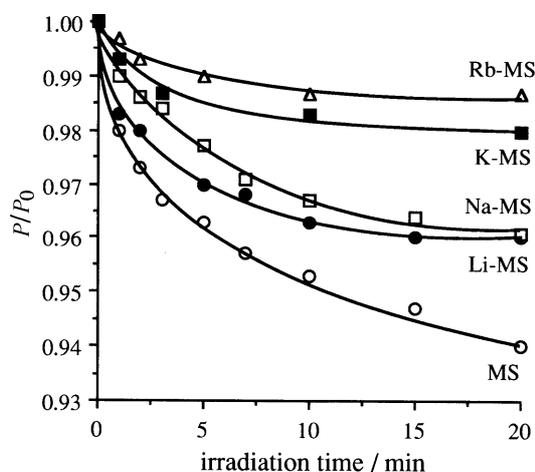


Fig. 3 Change in the pressure of CO on reduction of MS and alkali-metal ion modified MS samples by CO under UV irradiation at room temperature. P_0 , pressure of introduced CO; P , pressure of CO at each photoirradiation time.

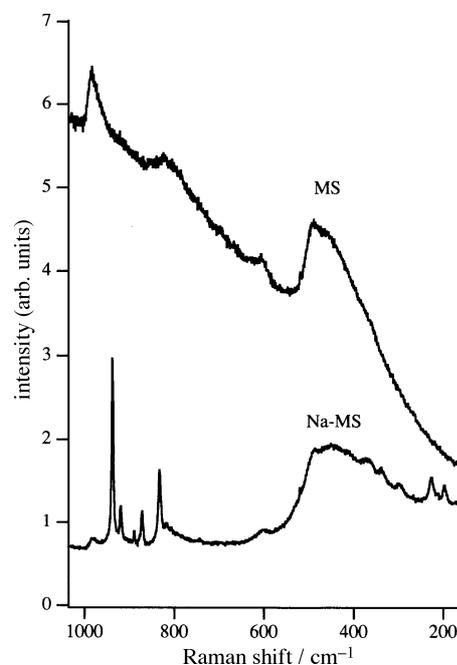


Fig. 4 Raman spectra of MS and Na-MS

ions. The small band at 888 cm⁻¹ could be assignable to Na₂MoO₄,²⁵ suggesting that a small amount of Na₂MoO₄ is present in Na-MS.

We carried out photooxidation of propane by ¹⁸O₂ over Na-MS at room temperature, with subsequent treatment of the Na-MS by ¹⁶O₂ at 673 K, and we then recorded the Raman spectrum of the Na-MS sample. The spectrum is shown in Fig. 5. In the Raman spectrum [Fig. 5(b)] of Na-MS used in photooxidation of propane with ¹⁸O₂, four of the bands (not the band at 888 cm⁻¹) were shifted to lower wavenumbers by *ca.* 5 cm⁻¹ and the bandwidths became broader than those [Fig. 5(a)] for Na-MS before use in the reaction. In the oxidation of propane by ¹⁸O₂, propanone was formed mainly and the content of ¹⁶O atoms contained in the propanone formed was higher than that of ¹⁸O atoms in the initial period of the reaction. The formation of ¹⁶O¹⁸O or ¹⁶O₂ was not confirmed during photooxidation, suggesting that the lattice oxygen in Na-MS was not exchanged for gaseous oxygen under these conditions. We also recorded the Raman spectra of Na-MS treated by ¹⁸O₂ at 673 K, and Na-MS irradiated by the light from an ultrahigh pressure Hg lamp in the

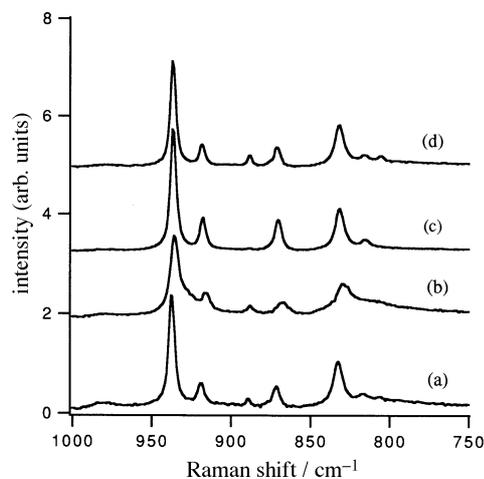


Fig. 5 Raman spectra of Na-MS samples. (a) Na-MS after pretreatment (described in Experimental section). (b) Na-MS used in photooxidation of propane by ¹⁸O₂ and successively treated by ¹⁶O₂ at 673 K. (c) Na-MS treated by ¹⁸O₂ at 673 K. (d) Na-MS irradiated by UV light in the presence of ¹⁸O₂.

presence of $^{18}\text{O}_2$ at room temperature. The spectra of the Na-MS samples were the same as the spectrum [Fig. 5(a)] of the Na-MS before use in the reaction by $^{18}\text{O}_2$. The results suggest that the lattice oxygen of the molybdenum species in Na-MS is not exchanged with gaseous oxygen by the treatment at 673 K or by irradiation with UV light at room temperature. Therefore, the band shift observed after photooxidation of propane with $^{18}\text{O}_2$ was caused by the interaction of the reactants (C_3H_8 and $^{18}\text{O}_2$) with the molybdenum species active for the reaction, *i.e.*, the lattice oxygen in the molybdenum species in Na-MS was incorporated into the propane and was then restored by gaseous oxygen during photooxidation of propane. From the results mentioned above, we conclude that the molybdenum species that gives the Raman bands at 936, 918, 870, and 830 cm^{-1} is the species active for photooxidation of propane. Na_2MoO_4 on silica would be inactive for the photooxidation, because the band at 888 cm^{-1} , due to Na_2MoO_4 , was not shifted after the photooxidation of propane by $^{18}\text{O}_2$.

Discussion

In the photooxidation of propane and propene, we found that the addition of alkali-metal ions to MS brought about a change in the photocatalytic performance, in particular, in selectivity. Over MS, a variety of products were formed, *i.e.*, the reaction over MS was not selective. However, the formation of propane from propene, and that of acrolein from propene became significant on the addition of alkali-metal ions to MS, *i.e.*, alkali-metal ion modified MS samples are effective at putting an oxygen atom into the hydrocarbons without the fission of C—C bonds. The same phenomena were also observed in photooxidation of light alkanes over alkali-metal ion modified $\text{V}_2\text{O}_5/\text{SiO}_2$ samples.^{9–12} It has been reported that the species active for photooxidation of propane over $\text{MoO}_3/\text{SiO}_2$ is an isolated molybdenum species in the triplet state formed by photoirradiation.²⁶ The excitation from the ground state to the triplet state was assigned to a charge-transfer transition from the oxygen atom to the molybdenum atom of $\text{Mo}=\text{O}$ in the surface molybdenum species. It is expected that the oxygen atom of the $\text{Mo}=\text{O}$ in the triplet state has a strong electrophilicity, such as is the nature of O^- , and the oxygen is active in the photooxidation of hydrocarbons because an electron from the oxygen atom in $\text{Mo}=\text{O}$ is transferred to the molybdenum atom by the excitation from the ground state to the triplet state. As the addition of alkali-metal ions to MS brought about a change in the catalytic performance for photooxidation, the alkali-metal ions would be located adjacent or close to the molybdenum species in the alkali-metal ion modified MS samples. In general, alkali-metal ions have a tendency to donate electrons. The electrophilicity of the oxygen of the $\text{Mo}=\text{O}$ in the excited molybdenum species is possibly weakened by the presence of alkali-metal ions, and consequently the catalytic performance for photooxidation should be changed. The differences in photocatalytic performance among the alkali-metal ion modified MS samples result from the distinction in their ability to donate electrons owing to the types of alkali-metal ions.

In the photo-assisted metathesis of propene, it was found that the addition of alkali-metal ions depressed the activity. The decrease in activity was correlated to the reducibility of the molybdenum species by CO under photoirradiation. Bañares *et al.* reported that the molybdate compounds formed upon addition of alkali-metal ions to $\text{MoO}_3/\text{SiO}_2$ were less reducible than the dispersed surface molybdenum species in $\text{MoO}_3/\text{SiO}_2$.⁸ Martin *et al.* also stated that the reducibility of the molybdenum species in $\text{MoO}_3/\text{TiO}_2$ decreased on addition of sodium ions.²² These results were obtained by temperature programmed reduction (TPR). The same phenomenon was found for reduction of molybdenum species

by CO under UV irradiation at room temperature. We suppose that one of the factors determining the reducibility is the energy level of the LUMO (lowest unoccupied molecular orbital) of the molybdenum species, because electrons would be incorporated into the LUMO in the reduction process. We have found that the energy levels of the LUMO and the HOMO (highest occupied molecular orbital) of the vanadium cluster are destabilized by the interaction of an alkali-metal ion when calculated by density functional theory,¹⁴ this is because of the donation of the electron from the alkali-metal ion to the vanadium cluster. For molybdenum species modified by alkali-metal ions, the same phenomenon occurs.

The structures of the molybdenum species in MS and alkali-metal ion modified MS were investigated by Raman spectroscopy. In the Raman spectrum of MS, a band was observed at 986 cm^{-1} but bands assigned to MoO_3 (995 and 820 cm^{-1})²⁷ and $\text{Mo}-\text{O}-\text{Mo}$ (deformation mode observed at 180–240 cm^{-1})²⁷ were not detected. The results indicate that the molybdenum species on silica is isolated, *i.e.*, monomeric in MS. There are many reports that the surface molybdenum species is tetracoordinated ($\text{O}=\text{Mo}=\text{O}$) O_2 at a low loading of MoO_3 in $\text{MoO}_3/\text{SiO}_2$ in a dehydrated state.^{27–30} However, it has been proposed that the structure of a dispersed surface molybdenum species in $\text{MoO}_3/\text{SiO}_2$ is octahedral in a dehydrated state.^{31–33} Hu *et al.* concluded from the results of Raman spectra and Mo $L_{3\text{-edge}}$ XANES that the surface molybdenum species on silica are isolated and highly distorted, and possess a symmetry somewhat between octahedral and tetrahedral coordination.³⁴ We can not determine the structure of the surface molybdenum species in MS by only the Raman spectrum.

On the other hand, bands different from those of MS were observed in the Raman spectrum of Na-MS. This indicates that with the addition of sodium ions alkali-metal–molybdate species are formed on the silica. In these bands of the Raman spectrum of Na-MS, a small band due to Na_2MoO_4 was identified, suggesting that the addition of sodium ions to MS brought about the formation of Na_2MoO_4 . However, we found that Na_2MoO_4 was inactive for photooxidation of propane and that the Raman band due to Na_2MoO_4 was not shifted by photooxidation of propane with $^{18}\text{O}_2$, while the other Raman bands were shifted to lower wavenumber during the reaction. Hence, the formation of Na_2MoO_4 is concluded to be independent of the change in the photocatalytic performance afforded by the addition of sodium ions to MS. The Raman bands of Na-MS at 936, 918, 870, and 830 cm^{-1} were similar to the bands due to $\text{Na}_2\text{Mo}_2\text{O}_7$ (940, 920, 880, and 820 cm^{-1}).³⁵ The Raman bands were shifted by the photooxidation of propane with $^{18}\text{O}_2$, suggesting that the molybdenum species that gave rise to them were the active species for the photooxidation and the formation of the molybdenum species caused the change in the photocatalytic performance. The structure of the molybdenum species can not only be determined by the Raman spectra. We expect from the results of the reactions in the present study that the different molybdenum species formed are dependent on the type of alkali-metal ions added and/or the amount added. In the future, we will describe the structures of the molybdenum species in the MS and alkali-metal ion modified MS samples by combining these results with those of other spectroscopic methods.

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