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Selective Photooxidation of Light Alkanes to Oxygenates using Supported Molybdenum Oxide Catalysts

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Photo-assisted catalytic partial oxidation of methane, ethane and propane has been performed in the presence of supported molybdenum oxide catalysts at around 500 K by the use of a fluidized bed flow-type reactor under UV irradiation. Temperatures as high as 500 K were indispensable for the selective formation of methanal from methane (*ca.* 19 µmol h^{-1}), corresponding to 5.5% of the photons irradiated into the catalyst bed (<300 nm). The yields were greatly affected by the loading levels of molybdenum species, the preparation methods of the catalysts and the light flux into the catalyst bed. Photooxidation of ethane and propane also selectively gave the corresponding aldehydes and ketones in high yields (*ca.* 80 µmol h^{-1}) at elevated temperature. The reaction seemed to proceed *via* charge-transfer complexes formed by photo-activation of terminal coordinatively unsaturated M=O groups in multilayers of molybdenum species.

Although the direct catalytic conversion of light alkanes has attracted much attention for many years, few attempts to convert methane and ethane directly into oxygen-containing chemicals with high conversions and high selectivities have been successful.[1–3] Since the functionalization of the unactivated C—H bond in light alkanes, especially methane, is very difficult, most of the known processes for utilization of these alkanes require very severe conditions to be generally non-selective.

As one of the techniques to overcome these barriers, photo-assisted catalytic oxidation of methane or ethane over solid oxide catalysts have been studied extensively for the last two decades using supported metal oxide catalysts or n-type solid oxide semiconductors.[4–11] Kaliaguine *et al.*[4] reported that methane and ethane reacted with hole centres generated by γ-irradiation of metal complexes (*e.g.* $V^{5+}—O^{-}$) dispersed on silica to form carbon oxides as the main products together with a small amount of methanal. Ward *et al.*[6] reported that the photooxidation of methane using silica-supported MoO_3 or $CuMoO_4$ catalysts at 313–373 K selectively yielded a small amount of methanol without deep oxidation, but the formation of methanal was not confirmed. Grätzel and co-workers[8,9] reported that elevated temperature, 473 K, enhanced the formation of carbon monoxide in place of carbon dioxide by photooxidation of methane using titanium dioxide-based catalysts. Photooxidation of propane using the supported molybdenum oxide catalysts has been investigated extensively by Kaliaguine and co-workers, usually at ambient temperature,[12,13] but the undesirable formation of large amounts of carbon oxides was inevitable. Recently, theoretical studies have been performed.[6,14]

Our previous reports demonstrated that methane and ethane are selectively converted into the corresponding aldehydes by photooxidation at elevated reaction temperatures using silica-supported molybdenum oxide catalysts.[15–17] The present paper focused on the more detailed study of effects of the reaction conditions, the preparation method of the catalysts and especially the correlation between catalytic activities and the surface state of the catalyst. Possible reaction mechanisms are also discussed.

Experimental

Materials

Typical silica-supported molybdenum oxide catalysts were prepared by the usual pore volume impregnation method (incipient wetness method, hereafter designated as MoO_3/SiO_2-IW(6), the number in the parentheses being the pH of the impregnating solution). Silica gel (Alfa, surface area 300 m^2 g^{-1}, mean particle size 10 µm, pore volume 1.6 cm^3 g^{-1}), γ-alumina (Nishio), low alumina (Shokubai Kasei, alumina 13%) or high alumina (Shokubai Kasei, alumina 29%) were impregnated overnight in an aqueous solution of ammonium heptamolybdate followed by vacuum evaporation at 323 K. The pH of the pristine solution was 6. When necessary, the pH was adjusted to 1 or 11 by adding an aqueous solution of HNO_3 or NH_4OH. The dried catalyst was then calcined in air at 823 K for 2 h. Other MoO_3/SiO_2 catalysts were prepared by the following equilibrium adsorption method [-EQ(5.5)]. The support (2 g) was impregnated in 100 cm^3 of an aqueous solution of ammonium heptamolybdate (0.007 mol dm^{-3}) for 72 h with vigorous stirring. The pH of the solution was adjusted with dilute HNO_3 and NH_4OH solutions. The solid was filtered off, washed with distilled water and calcined in air at 823 K for 2 h. The MoO_3/SiO_2-VD catalyst was prepared as follows: $Mo(CO)_6$ adsorbed on silica gel was prepared by the introduction of $Mo(CO)_6$ vapour into the vessel containing dried silica gel at room temperature. It was then subjected to UV irradiation in a stream of air for 30 min at room temperature followed by calcination in air at 823 K for 2 h. Since some of molybdenum oxide of these catalysts was reported to be lost during calcination in air at temperatures >823 K,[1] the amount of molybdenum contained in these catalysts after calcination was measured by atomic absorption analysis, in which molybdenum oxide was leached out with NH_4OH solution. All the catalysts mounted in the reaction apparatus were again subjected to calcination in a stream of air at 823 K for 2 h.

Highly purified methane (>99.9%, <0.01% of ethane) was used without any further purification. The ethane, including a small amount of CO_2 and water vapour, was slowly passed over a column filled with pulverized fused potassium hydroxide and 5A molecular sieves, and then fed to the reactor. Propane, helium and oxygen were used as received.

Apparatus and Procedures

The reaction was carried out using an upstream flow-type reactor equipped with a preheater and a window for UV irradiation (10 mm × 20 mm; inner thickness 1 mm), as described before.[15] This system included a fluidized catalyst bed in order to irradiate all the catalyst particles. The reactant gas mixture was passed through the preheater (maximum temperature; 823 K) to maintain the temperature of the catalyst bed. There were variations in the temperature of *ca.* 15 K between the top and the bottom of the catalyst bed. UV irradiation was performed using three types of high-pressure mercury vapour lamps with water filters; 200 W (arc length; 150 mm, hereafter designated as lamp A), 75 W (15 mm, lamp B) and 200 W (75 mm, lamp C). Chemical actinometry using iron(III) oxalate revealed that the number of photons irradiated into the catalyst bed using lamp C was 3.3×10^{-7} einstein s^{-1} (250–500 nm, 0.9×10^{-7} einstein s^{-1} for 250–300 nm). The relative intensity of the light flux was about 1 : 1 : 3 for lamps A : B : C (values contained errors of *ca.* 20%). The reaction was carried out typically with 0.025 g of the catalyst and 7.5 mmol h^{-1} of alkane. The details of the reaction conditions are listed in Table 1. The liquid and gaseous products were collected in cold traps and gas-sampling bags, respectively.

Analysis

The products were analysed by gas chromatography: a Porapak-Q column at 353 K with an FID for C_1–C_4 hydrocarbons and at 433 K for methanol, ethanal and ethanol; a Porapak-N column at 433 K with an FID for acetone and propanal; a TSG-1 on Shimarite-F column, distributed from Shimadzu Co. Ltd., at 393 K with a TCD for methanal; a 5A molecular sieve column at 323 K with a TCD for oxygen; and an active carbon column at 323 K with a TCD for H_2, CO and CO_2.

An atomic absorption analysis was carried out using an AA-8200 atomic absorption/flame emission spectrometer (Nippon Jarrell Ash Inc.). The BET surface area of the catalysts was measured with a BELSORP 28, a microprocessor-controlled automatic system using N_2 at 77 K, from BEL Japan Inc. An X-ray diffraction study was performed using a RIGAKU Geigerflex with Kα-emission of copper in the range $5° < 2\theta < 70°$. UV–VIS diffuse reflectance spectra were measured with a Shimadzu model MPS-2000 multipurpose spectrophotometer, in which reflected beams were gathered by an integrating sphere (50 mm id). A UV cell (10 mm × 40 mm, 1 mm inner thickness) equipped with a branched chamber and a stop valve was used in order to avoid any contact with moisture. The catalyst submitted for the measurement was heated in the branched chamber at 573 K under atmospheric pressure for 30 min, then evacuated at 823 K for 30 min followed by the treatment under 150 Torr of oxygen at 823 K for 2 h. Then the catalyst was transferred into the UV cell and measured *in vacuo*. Magnesium oxide (Wako) was used as a reflectance standard. All the spectra are modified in terms of the Kubelka–Munk function.[18]

XPS (X-ray photoelectron spectroscopy) spectra of the MoO_3/SiO_2 catalysts were acquired using a Perkin-Elmer 5500 MT system equipped with a hemispherical energy analyser. The catalyst pretreated in air at 823 K for 2 h was mounted on indium foil and then transferred to an XPS analyser chamber. The residual gas pressure in the chamber during data acquisition was $<1 \times 10^{-8}$ Torr. XP spectra were measured at room temperature using Mg-$K\alpha_{1,2}$ radiation (15 kV, 400 W). The extent of dispersion of supported molybdenum species was estimated on the basis of relative peak area intensities of Mo 3p (398.2 eV), Mo $3d_{5/2}$ (232.7 eV), Mo $3d_{3/2}$ (235.9 eV), Si 2p (103.3 eV), O 1s (531.1 eV) and C 1s (285.0 eV). The electron take-off angle was set at 45°. The spectral accumulation time was *ca.* 40 min for Mo 3p and 10 min for Si 2s. Binding energies were referenced to the Si 2p level for the catalyst support, SiO_2.

Table 1 Typical reaction conditions for the photooxidation of light alkanes

alkane	CH_4	C_2H_6	C_3H_8
amount of catalyst/g	0.025	0.025	0.025
alkane feed rate/mmol h^{-1}	7.5	7.5	7.5
alkane : O_2 : He	6 : 2 : 25	6 : 1 : 21	3 : 1 : 10
W/F^a/g h mol^{-1}	0.62	0.71	0.71
SV^b/h^{-1}	10000	8200	8200
content of the cold trap	water	acetone	methanol
temperature of the trap/K	273	195	195

[a] Weight of the catalyst divided by the total feed of the reaction gas. [b] Space velocity.

Results

Effects of the Catalyst Preparation Conditions on the Photooxidation of Methane

Table 2 shows the results of the photooxidation of methane at 463–503 K on various supported molybdenum oxide catalysts during the first 120 min. Loading levels of MoO_3 onto SiO_2 support in the following tables and figures are those based on the atomic absorption analysis. Blank reactions in the absence of the catalyst at a preheater temperature of 823 K with or without UV irradiation did not give any products, indicating that oxidation in the dark on the reactor wall and photochemical reactions can be ruled out. The reaction using silica gel showed that only a trace of methanal obtained in the catalytic run was due to the support.

Table 2 Photoinduced partial oxidation of methane on various supported molybdenum catalysts[a]

run	catalyst	cat. wt./g	loading (wt.%)	T/K	yield/μmol h^{-1}	
					HCHO	MeOH
1	none[b,c]	—	—	—	n.d.	n.d.
2	none[c]	—	—	—	n.d.	n.d.
3	SiO_2[d]	0.050	—	463	trace	n.d.
4	MoO_3/SiO_2-IW(6)	0.025	4.4	493	5.8	0.2
5	MoO_3/low alumina	0.025	5.0[e]	473	trace	n.d.
6	MoO_3/high alumina	0.025	5.0[e]	503	trace	trace
7	MoO_3/Al_2O_3	0.025	5.0[e]	493	trace	trace
8	$H_3PMo_{12}O_{40}/SiO_2$[d]	0.050	10[e]	493	2.2	0.4
9	MoO_3	0.180	—	503	trace	n.d.
10	Na_2MoO_4	0.250	—	493	trace	n.d.

[a] CH_4 feed rate 7.5 mmol h^{-1}, CH_4 : O_2 : He 6 : 2 : 25, no trace of carbon dioxide was detected, lamp A (200 W, arc length 150 mm), n.d. not detected. [b] Without UV irradiation. [c] Furnace temperature 823 K. [d] CH_4 : O_2 : He 2 : 3 : 17. [e] Calculated from the amount of Mo in the impregnating solution.

The silica-supported molybdenum oxide catalyst (4.4 wt.%) afforded 5.8 μmol h^{-1} [0.75 mol (Mo mol $h)^{-1}$] of methanal together with 0.2 μmol h^{-1} of methanol. The colour of the catalyst remained white during the reaction. The products were methanal and methanol and no trace of oxides of carbon was observed. Formic acid was not detected by GC analysis. The experiments on the effect of the reaction temperature showed that the yield of methanal increased markedly above 440 K and then levelled off at around 450–500 K.[15] Although Ward *et al.*[6] reported the production of methanol at around 318 K on MoO_3/SiO_2, the reaction in our study at 320 K gave none of the products. After reaction at 320 K for 60 min, the catalyst bed temperature was raised to 823 K in a stream of argon, but no oxygen-containing chemicals were evolved.

Molybdenum oxide loaded on a different support, such as low alumina, high alumina or γ-alumina, did not afford significant amounts of products, indicating a strong interaction between molybdenum species and the support. Heteropolyoxyanions such as $PMo_{12}O_{40}^{3-}$ are known to be photoactive towards the oxidation of alcohols and alkanes.[8] In our study, a silica-supported $H_3PMo_{12}O_{40}$ (10 wt.%) catalyst gave methanal with a yield of 2.2 μmol h^{-1}. On the other hand, bulk MoO_3 or Na_2MoO_4 did not show any catalytic activity.

As shown in Fig. 1, the yield of methanal changed with the loading level of MoO_3. The 2.5 wt.% loaded -IW catalyst afforded the maximum yield of methanal, and further increase in the loading of MoO_3 decreased its yield. Then we compared the activities of the silica-supported MoO_3 catalysts prepared by different methods. As shown in runs 11–13 of Table 3, both the catalysts impregnated from an acidic and a basic solution contained smaller amounts of MoO_3 and afforded methanal in lower yields than the catalyst prepared from the solution of pH 6. With the catalysts prepared by the equilibrium adsorption method, the loading levels of MoO_3 decreased in following order, pH 1 (1.8 wt.%) > 5.5 (1.2 wt.%) > 11 (0.7 wt.%). The catalyst prepared at pH 1 was one of the best catalysts to give methanal selectively in a yield of 4.4 μmol h^{-1}, 1.4 mol (Mo mol $h)^{-1}$), whereas the catalyst prepared at pH 5.5 showed the highest intrinsic activity [the yield per unit Mo, 1.7 mol (Mo mol $h)^{-1}$]. The molybdenum species on the catalyst prepared at pH 11 was inferior in its intrinsic activity, 0.6 mol (Mo mol $h)^{-1}$. The MoO_3/SiO_2 catalyst prepared by the adsorption of $Mo(CO)_6$ vapour, including 1.8 wt.% of MoO_3, was also inferior in its activity per unit Mo.

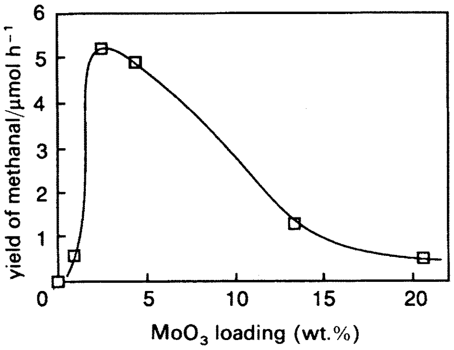


Fig. 1 Yield of methanal at 463 K over MoO_3/SiO_2-IW(6) catalysts of various loading levels using lamp A (200 W). Amount of catalyst 0.025 g, CH_4 feed rate 7.5 mmol h^{-1}, $CH_4 : O_2 : He$ 6 : 2 : 25, *W*/*F* 0.62 g h mol^{-1}.

Table 3 Effect of the preparation methods of the silica supported MoO_3 catalysts[a]

run	preparation	loading (wt.%)	*T* /K	yield/μmol h^{-1} HCHO	MeOH
11	IW(1)	2.9	473	2.5	0.2
12	IW(6)	4.4	463	4.9	0.2
13	IW(11)	2.6	473	2.6	0.2
14	EQ(1)	1.8	473	4.4	0.3
15	EQ(5.5)	1.2	473	3.6	trace
16	EQ(11)	0.7	473	0.7	n.d.
17	VD	1.8	493	2.7	0.2

[a] Amount of catalyst 0.025 g, *W*/*F* 0.62 g h mol^{-1}, space velocity 10 000 h^{-1}, CH_4 feed rate 7.5 mmol h^{-1}, $CH_4 : O_2 : He$ 6 : 2 : 25, no trace of carbon dioxide was detected, lamp A, n.d. not detected.

Table 4 summarizes the effects of several reaction parameters *e.g.* intensity of UV irradiation. The reaction did not take place at all without UV irradiation at 523 K. It is suggested that a wavelength shorter than 300 nm is required to activate the MoO_3/SiO_2 catalyst by the reaction with UV irradiation through a Pyrex filter (passes >300 nm). The highest yield of methanol [19 μmol h^{-1}, 2.5 mol (Mo mol $h)^{-1}$] was obtained at 503 K together with 6 μmol h^{-1} of carbon monoxide from lamp C with a light flux three times as great as that for lamps A and B. Provided that the reaction requires one photon to produce one molecule of methanal from methane, this methanal yield corresponds to 5.5% of the photons (<300 nm) irradiated into the catalyst bed. Carbon monoxide would be formed by the decomposition of methanal. Since the yields of methanal were almost constant at 450–500 K,[15] these results suggest that the yields of the products increased almost in proportion to the intensity of light flux into the catalyst bed. We have also tried to examine the benefit of fluidization of the catalyst bed by restricting the movement of the catalyst particles using a quartz wool plug (run 21). The apparent irradiation area was reduced by half. The yield of methanal was reduced to 2.2 μmol h^{-1}, indicating that fluidized catalyst bed is advantageous by virtue of increasing the irradiation area.

Effects of Reaction Conditions on the Photooxidation of Ethane

The photooxidation of ethane was examined on the MoO_3(2.5 wt.%)/SiO_2-IW(6) catalyst, one of the most active catalysts toward the reaction with methane (see above). The results for the first 60 min are shown in Table 5. Although *W*/*F* was higher than that with methane oxidation, the apparent irradiation area of the fluidized catalyst bed was

Table 4 Photo-assisted partial oxidation of methane using the MoO_3(4.4 wt.%)/SiO_2-IW(6) catalysts[a]

run	lamp	*T* /K	yield/μmol h^{-1} HCHO	MeOH	CO
18	—	523	n.d.	n.d.	n.d.
3	A	493	5.8	0.2	n.d.
19[b]	A	463	2.8	0.2	n.d.
20[b,c]	A	463	trace	n.d.	n.d.
21[d]	A	473	2.2	trace	n.d.
22	C	483	11	0.4	n.d.
23	C	503	19	0.7	6

[a] Amount of catalyst 0.025 g, *W*/*F* 0.62 g h mol^{-1}, space velocity 10 000 h^{-1}, CH_4 feed rate 7.5 mmol h^{-1}, $CH_4 : O_2 : He$ 6 : 2 : 25, n.d. not detected, no trace amount of carbon dioxide was detected. [b] Amount of catalyst 0.050 g, $CH_4 : O_2 : He$ 2 : 3 : 17, amount of loaded MoO_3 7.9 wt.%. [c] Irradiated through the Pyrex filter. [d] Fixed catalyst bed.

Table 5 Selective photooxidation of ethane using the MoO_3(2.5 wt.%)/SiO_2-IW(6) catalyst[a]

run	lamp	cat. wt. /g	T /K	yield/μmol h^{-1} CH_3CHO	C_2H_5OH	HCHO	CO	CO_2
24	—	0.025	483	n.d.	n.d.	n.d.	n.d.	trace
25	B	0.025	463	14	0.7	4.0	n.d.	trace
26	B	0.014	463	6.6	0.7	1.6	n.d.	n.d.
27	B	0.051	463	17	1.2	3.2	n.d.	4
28	C	0.025	493	38	3.1	20	trace	7
29[b]	C	0.025	493	60	2.3	22	trace	5

[a] Amount of catalyst 0.025 g, W/F 0.71 g h mol^{-1}, space velocity 8200 h^{-1}, ethane feed rate 7.5 mmol h^{-1}, $C_2H_6 : O_2 :$ He 6 : 1 : 21, n.d. not detected. [b] Ethane feed rate 19 mmol h^{-1}, oxygen feed rate 2.5 mmol h^{-1}.

almost unchanged. The products were ethanal and methanal together with small amounts of ethene, ethanol and carbon dioxide. The formation of acetic acid was not observed by GC analysis. The reaction without a catalyst at a preheater temperature of 823 K gave only a trace of carbon dioxide and none of the oxygen-containing chemicals. The reaction without UV irradiation using the MoO_3/SiO_2 catalyst gave none of the oxygenates.

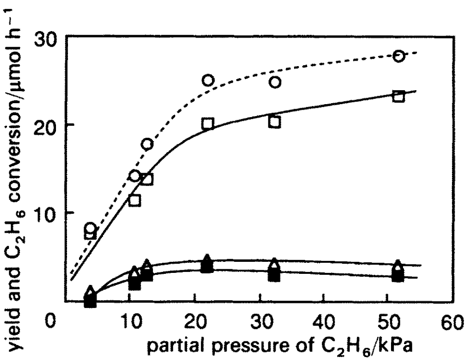


Fig. 2 Effect of partial pressure of ethane over the MoO_3 (2.5 wt.%)/SiO_2-IW(6) catalyst on ethane conversion (○), yield of ethanal (□), methanal (△) and CO_2 (■) at 473 K using lamp B (75 W), P_{oxygen} = 7.2 kPa.

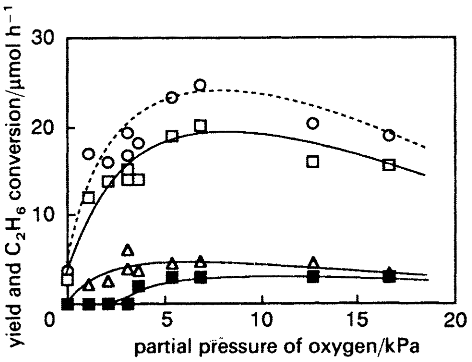


Fig. 3 Effect of partial pressure of oxygen using the MoO_3 (2.5 wt.%)/SiO-IW(6) catalyst on ethane conversion (○), yield of ethanal (□), methanal (△) and CO_2 (■) at 473 K using lamp B (75 W), P_{ethane} = 22 kPa.

Under irradiation using lamp B, 14 μmol h^{-1} of ethanal and 4.0 μmol h^{-1} of methanal together with small amounts of ethanol and carbon dioxide were formed. The selectivity for useful oxygen-containing chemicals was >90%. The activity did not change during a prolonged run of 5 h. Similar to the case with methane, the reactions of ethane at various catalyst bed temperatures under UV irradiation revealed that the formation of ethanal was markedly enhanced above 400 K and then levelled off at around 475–500 K. Only 1.2 μmol h^{-1} of ethanal was obtained without preheating using lamp A.[16] We examined the presence of adsorbed species on the surface of the catalyst by raising the catalyst bed temperature to 823 K under a flow of argon, but none of the desorbed products were observed from the used catalyst after the reactions in the dark or without preheating. From the catalyst after the reaction at around 500 K for 60 min, a very small amount of carbon dioxide (<0.5 μmol) was formed together with ethane. A trace of ethene was also evolved.

The apparent UV irradiation area decreased in proportion to the amount of the catalyst for <0.025 g catalyst, whereas it slightly increased with 0.051 g of the catalyst. The reaction using various amounts of the catalyst revealed that the yields of the products depended not on the weight but on the apparent irradiation area of the catalyst (see runs 25–27).

When the light flux into the catalyst bed was increased by the use of lamp C, the yields of the products increased. Ethanal and methanal were formed at 493 K with yields of 38 and 20 μmol h^{-1}, respectively. Owing to optimization of the reaction conditions, the highest yields of ethanal (60 μmol h^{-1}) and methanal (22 μmol h^{-1}) with high selectivity (over 96%) for oxygen-containing compounds was achieved.

We examined the effects of partial pressure of the reactant in the reaction mixture on the MoO_3(2.5 wt.%)/SiO_2-IW(6) catalyst. Fig. 2 shows the yields of the products and the ethane conversions at various partial pressure of ethane, P_{ethane}, with constant partial pressures of other components. The conversion of ethane increased markedly with increasing P_{ethane} up to *ca.* 20 kPa and then gradually at higher P_{ethane}. With increasing P_{oxygen} up to *ca.* 5 kPa, ethane conversion and yields of ethanal markedly increased (Fig. 3). With further increase in P_{oxygen}, conversion of ethane and the

Table 6 Selective photooxidation of propane using the MoO_3(2.5 wt.%)/SiO_2-IW(6) catalyst[a]

run	lamp	T /K	yield/μmol h^{-1} C_2H_5CHO	$(CH_3)_2CO$	CH_3CHO	CO	CO_2
30	—	550	n.d.	n.d.	n.d.	n.d.	trace
31	B	471	8.1	5.0	6.3	n.d.	1
32	B	516	10	7.0	6.1	n.d.	3
33	C	493	15	9.8	15	n.d.	3
34[b]	C	493	16	10	16	n.d.	3

[a] Amount of catalyst 0.025 g, W/F 0.71 g h mol^{-1}, ethane feed rate 7.5 mmol h^{-1}, $C_3H_8 : O_2 :$ He 3 : 1 : 10, space velocity 8200 h^{-1}, n.d. not detected. [b] Prolonged run of 6–7 h.

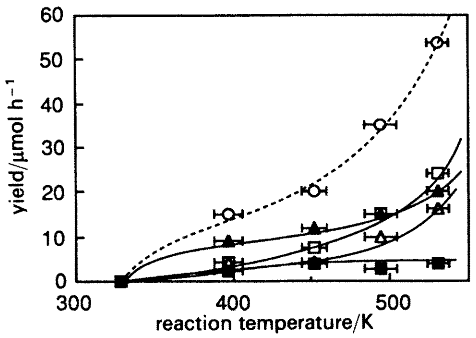


Fig. 4 Photooxidation of propane at various catalyst bed temperatures using the MoO_3 (2.5 wt.%)/SiO_2-IW(6) with lamp C (200 W). Amount of catalyst 0.025 g, C_3H_8 feed rate 7.5 mmol h^{-1}, $C_3H_8 : O_2 :$ He 3 : 1 : 10, W/F 0.71 g h mol^{-1}. Yields of (□) propanal, (△) acetone, (▲) acetaldehyde, (■) CO_2, and (○) C_3H_8 conversion.

yields of aldehydes gradually decreased. Note that deep oxidation of ethane to carbon oxides was not enhanced by increasing P_{oxygen} above 5 kPa. On the other hand, the reaction in the absence of oxygen yielded 2.7 µmol h^{-1} of ethanal together with small amounts of ethene and ethanol during the first 60 min. The yields promptly decreased with time on stream. After the reaction without molecular oxygen for several hours, the colour of the catalyst changed to greyish blue–green.

Photooxidation of Propane

Photooxidation of propane on the MoO_3/SiO_2 catalysts has been performed by Marcinkowska and co-workers[12,13] at ambient temperature, and they reported the formation of ethanal, propanal and acetone together with large amounts of CO and CO_2. The reaction resulted in low selectivity for useful products.

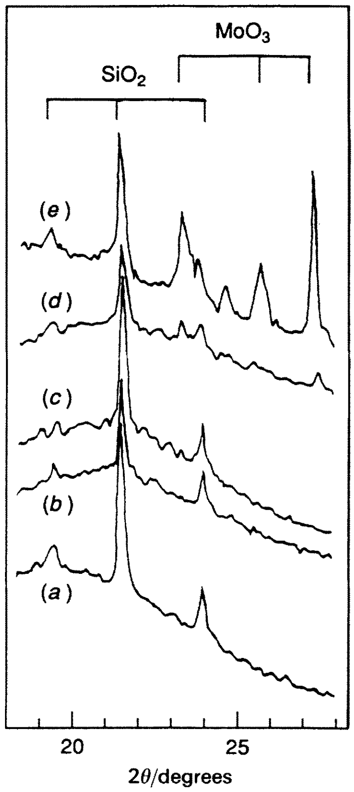


Fig. 5 XRD patterns and BET surface areas of the MoO_3/SiO_2-IW(6) catalysts with various loading levels: (*a*) 0.9 wt.%, 185.5 m^2 g^{-1}, (*b*) 2.5 wt.%, 187.3 m^2 g^{-1}; (*c*) 4.4 wt.%, 175.1 m^2 g^{-1}; (*d*) 13 wt.%, 149.3 m^2 g^{-1}; (*e*) 21 wt.%, 131.4 m^2 g^{-1}

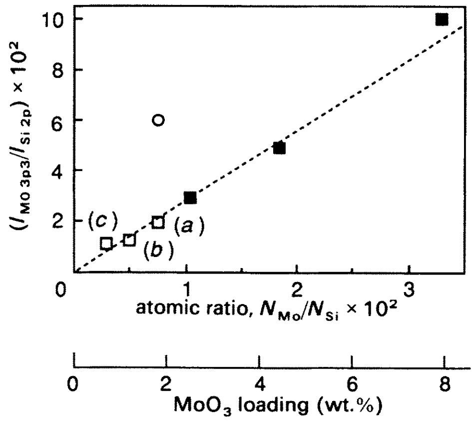


Fig. 6 XPS intensity ratio $I_{Mo\,3p3}/I_{Si\,2p}$ as a function of overall atomic ratio of Mo and Si of the MoO_3/SiO_2 catalysts prepared by (■) the impregnation method at pH 6, (□) the equilibrium adsorption method [pH of impregnating solutions: (*a*) 1, (*b*) 5.5, (*c*) 11], (○) from $Mo(CO)_6$-adsorbed silica.

We examined the photooxidation of propane as well as methane and ethane at elevated temperature on the MoO_3(2.5 wt.%)/SiO_2-IW(6) catalyst (Table 6). The products were propanal, acetone and ethanal together with small amounts of methanal and carbon dioxide. The formation of carbon monoxide, propanol and carboxylic acids was not observed by GC analysis. None of the products was obtained in the reaction without UV irradiation. The reaction in the absence of the catalyst at the preheater temperature of 723 K gave only a trace of carbon dioxide.

Irradiation using lamp B at around 470 K gave *ca.* 20 µmol h^{-1} of the oxygen-containing products. The reaction using lamp C afforded the products in higher yields, *e.g.* 15 µmol h^{-1} of propanal, 9.8 µmol h^{-1} of acetone and 15 µmol h^{-1} of ethanal were formed at 493 K. Only 3 µmol h^{-1} of carbon dioxide was detected in the effluent gas, suggesting a high selectivity for the oxygen-containing products. The yields did not change during a prolonged run of 7 h.

Heating the catalyst bed to 823 K after the completion of the reaction for 3 h at 493 K afforded 0.7 µmol of carbon dioxide together with trace amounts of propene, ethane, ethene and unreacted propane. Ethanal, propanal and acetone were not desorbed.

Fig. 4 shows the yields of the products at various catalyst bed temperatures under UV irradiation using lamp C. Whereas only trace amounts of products were formed without preheating (319 K), the highest yields of propanal (24 µmol h^{-1}), acetone (16 µmol h^{-1}) and ethanal (20 µmol h^{-1}) were achieved at *ca.* 530 K. Note that ethanal, a C—C bond dissociated product, was formed at 400–450 K, a relatively low temperature, whereas predominant formation of methanal was observed in the photooxidation of ethane at higher temperature. The amount of carbon dioxide in the effluent gas did not exceed 5 µmol h^{-1}.

Catalyst Characterization

Fig. 5 shows the XRD patterns and surface areas of the MoO_3/SiO_2-IW(6) catalysts at various loading levels. A pattern common to all the samples could be identified as crystalline SiO_2. For the catalyst loaded with 13 wt.% of MoO_3, peaks attributed to crystalline MoO_3 appeared. These peaks developed further with increasing loading, indicating the formation of large crystallites of MoO_3 on the surface of the catalysts at loadings > 13 wt.%.

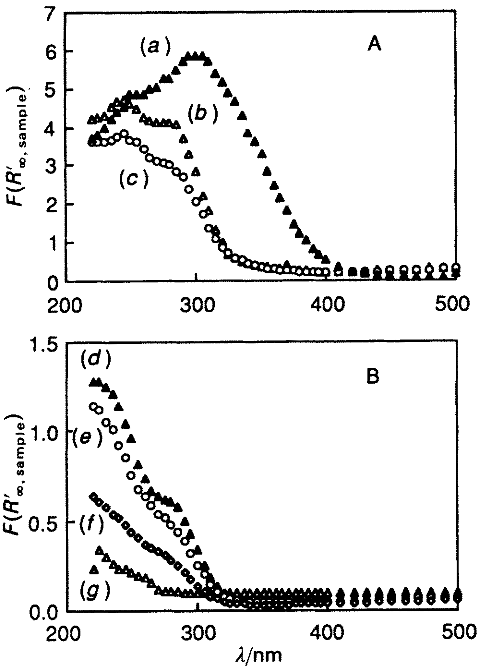


Fig. 7 UV diffuse reflectance spectra of the MoO_3/SiO_2 catalysts prepared by (A) the impregnation method at pH 6 of (*a*) 21 wt.%, (*b*) 4.4 wt.%, (*c*) 2.5 wt.% loading, and (B) equilibrium adsorption method from the solution at (*d*) pH 1, (*e*) pH 5.5, (*f*) pH 11. (*g*) SiO_2 support.

According to the relative ratio of XPS peak intensities of Mo 3p3 and Si 2s, I_{Mo3p3}/I_{Si2s}, *vs.* overall atomic ratio (N_{Mo}/N_{Si}) (Fig. 6), the catalysts prepared by the equilibrium adsorption method at pH 11 and the -VD catalyst showed higher observability of Mo than the -EQ(1), -EQ(5.5) and -IW(6) catalysts of various loading levels. Combined with the XRD analysis of Fig. 5, these results suggest the formation of multilayered molybdenum species on the surface even with the -EQ(1), -EQ(5.5) and -IW(6) catalysts of low Mo content, whereas the -EQ(11) and -VD catalysts seem to have more dispersed species on their surface.[17]

Fig. 7 shows the UV diffuse reflectance spectra of some of the silica-supported MoO_3 catalysts. A major absorption band around 240–250 nm together with a shoulder around 280 nm were detected for the MoO_3 (2.5 wt.%)/SiO_2-IW(6) catalyst (*c*) and the 4.4 wt.% loaded catalyst (*b*). On the other hand, the MoO_3 (21 wt.%) loaded catalyst exhibited a strong absorption band around 300 nm, in addition to that at 240 nm. Absorption at 280 nm was not confirmed on this catalyst. The spectra of the catalysts prepared by the equilibrium adsorption method from acidic and neutral solutions showed absorption bands around 240 and 280 nm, whereas the catalyst prepared at pH 11 showed very weak absorptions at 280 nm. Note that the moisture exposed MoO_3(2.5 wt.%)/SiO_2-IW catalyst showed a new strong absorption band at 320–330 nm.

Discussion

Correlation between the UV absorption λ_{max} and the coordination state of metal ions is generally accepted. The MoO_3(2.5 wt.%)/SiO_2-IW(6) catalyst showed absorption bands with maxima around 240 and 280 nm. Absorption bands around 240 and 280 nm have been assigned to $3t_2 \leftarrow 2t_1$ and $3t_2 \leftarrow t_1$ transitions, respectively, in the tetrahedrally coordinated molybdenum species.[19,20] Marcinkowska *et al.*[12] attributed the latter band to oxomolybdenum dimers or molybdenum ions in the terminal position of a polymeric layer and the band around 240 nm to monomeric molybdenum species. The absorption band at $\lambda > 300$ nm has often been attributed to Mo species in octahedral coordination.[19] The XRD study revealed the formation of large crystallites of MoO_3 on the surface of the MoO_3(21 wt.%)/SiO_2-IW(6) catalyst, and the band around 300 nm was observed with this catalyst.

Photooxidation of methane did not proceed without irradiation with $\lambda < 300$ nm. In Marcinkowska's study,[12] photooxidation of propane gave the products under UV irradiation of a wavelength > 280 nm. Provided that the catalyst was activated by light of a wavelength corresponding to its absorption band in the UV region, surface-active species would be provided from coordinatively unsaturated species at least having absorption bands at around 280 nm.

The results of the reactions with catalysts prepared by different methods gave information on the surface-active molybdenum species. The influence of pH in the impregnation on the structure and properties of MoO_3/SiO_2 has been studied extensively.[21–23] The molybdenum species prepared in an aqueous solution of ammonium heptamolybdate should be monomeric $MoO_4{}^{2-}$ under basic conditions, while a variety of polymeric species exist at a lower pH value:[24–26]

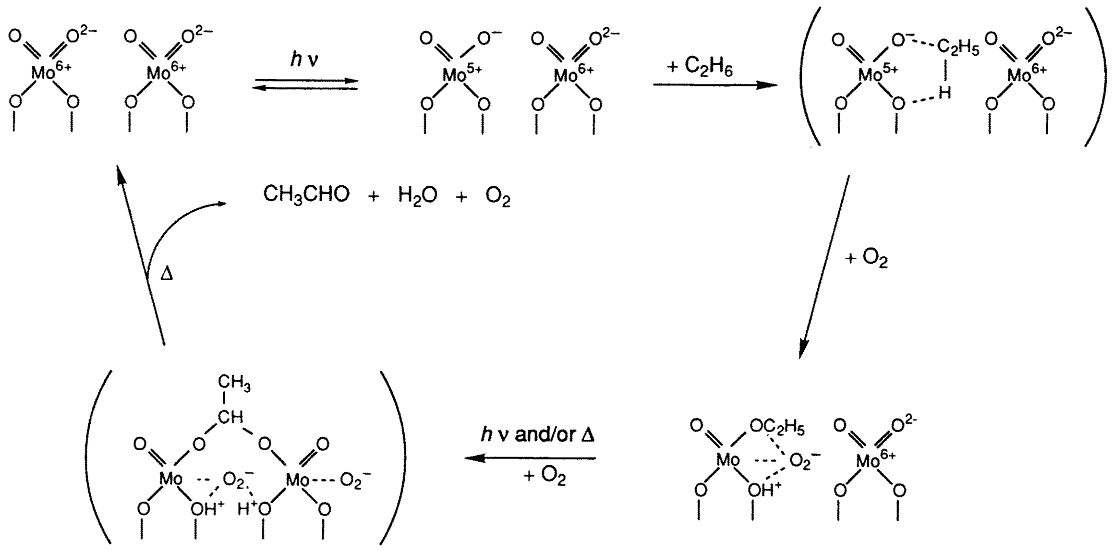
$$Mo_8O_{26}{}^{4-} + 2H_2O \rightleftharpoons (Mo_7O_{24})^{6-} + 3H^+ + HMoO_4{}^- \quad pH < 2 \qquad (1)$$

$$(Mo_7O_{24})^{6-} + 4H_2O \rightleftharpoons 7(MoO_4)^{2-} + 8H^+ \quad 2 < pH < 6 \qquad (2)$$

Monolayer-type molybdenum species are formed at low loading levels when the pH of the solution is lower than the isoelectric point of the support, typically pH 2 for silica.[27] The interaction between molybdate and silica is weak at high pH values. The formation of islands of molybdenum oxide has been proposed on the surface of the catalyst prepared from a neutral solution. These changes in the state of MoO_3 on the surface might affect photocatalytic reactions.

The catalysts prepared by the equilibrium adsorption method from a basic solution had more highly dispersed molybdenum species than those prepared from basic and neutral solutions according to the XPS study, but this catalyst did not show significant activity. On the other hand, catalysts prepared from the solution at lower pH contained more segregated MoO_3 species, and showed higher intrinsic activities. The results using the MoO_3/SiO_2-VD catalyst gave more distinct information. Although the XPS data of this catalyst showed its very high dispersity, its intrinsic activity was significant lower than the -IW(6), -EQ(1) or -EQ(5.5) catalysts. The intrinsic activity of the molybdenum species also depend on the loading levels of MoO_3. The MoO_3(2.5 wt.%)/SiO_2-IW(6) catalyst exhibited the maximum intrinsic activity. These results suggest that the active species would be the coordinatively unsaturated M=O species in the terminal position of less dispersed molybdenum species, but not large crystallites of MoO_3, which would be responsible for the absorption band at 280 nm.[12,13]

Gerasimov[11] showed that molecular oxygen could not be the direct source of CO_2, a sole product, by the photooxidation of methane with molecular oxygen on V^{5+}/SiO_2 at ambient temperature. A recent study on photooxidation of propene revealed the direct participation of lattice oxygen.[28] As described above, photooxidation of ethane in the absence of molecular oxygen selectively gave a small amount of ethanal during the initial stages. Thus it is reasonable to consider the source of oxygen in ethanal to be lattice oxygen from molybdenum oxide.



Scheme 1

A possible mechanism for photooxidation of ethane is illustrated in Scheme 1. This is based on the mechanism proposed by Kaliaguine *et al.*[4] for photo-assisted catalytic oxidation of light alkanes over a V^{5+}/SiO_2 catalyst at ambient temperature. The present mechanism requires doubly bonded surface $Mo^{6+}O^{2-}$ species. At the first step, surface $Mo^{6+}O^{2-}$ species is activated by light to form a charge-transfer complex, $Mo^{5+}O^{-}$. The reaction between alkane and the photoactivated O^{-} species leads to the activation of its C—H bond to form alkoxide-like intermediate species. At the same time, molecular oxygen is adsorbed onto a molybdenum ion which can provide an electron to promote charge separation. The alkoxide intermediate is swiftly converted into aldehydes and/or ketones under the present conditions. Our studies on photo- and catalytic oxidation of alcohols by molecular oxygen with MoO_3/SiO_2 catalysts revealed that alcohols can be selectively converted into aldehydes without UV irradiation at 493 K, although irradiation accelerates the reaction. This indicates that some aldehyde is formed from an alkoxide intermediate not only by photo-assisted oxidation but also by thermal catalytic oxidation. On the other hand, adsorbed molecular oxygen would re-oxidize the reduced surface to regenerate the original state. A similar mechanism has been proposed for propane oxidation.[12]

The most characteristic feature in our procedure is the irradiation at high temperatures. Higher temperatures primarily promote the desorption of the oxygenated products from the catalyst. At ambient temperature, the colour of the catalysts promptly turned blue during the reaction, probably due to 'molybdenum blue' species in the non-stoichiometric reduced state.[5] Bluish coloration was also observed after the reaction without molecular oxygen. Although adsorption of water or other species on the supported molybdenum oxide catalyst could change its colour, the catalyst seems to be partially reduced at lower temperature owing to a slow reoxidation process. Provided that the reaction proceeds mainly as shown in Scheme 1, the re-oxidation process includes simultaneous abstraction of another hydrogen from an activated alkane and cleavage of a metal–oxygen bond. It is reasonable that promotion of the rate of release of products and the rate of re-oxidation increases the turnover frequency of the overall reaction. The elevated temperature would affect the kind and/or life of the photoactivated surface species, but its nature is still unclear and is the next target of our study.

Conclusion

The selective photo-assisted catalytic oxidation of light alkanes to aldehydes, including the first example of selective formation of methanal from methane, has been achieved by the use of the MoO_3/SiO_2 catalysts at 450–500 K with UV irradiation. The 2.5 mol% loaded catalyst highly selectively gave methanal from methane in the highest yield of 19 μmol h^{-1}, corresponding to 5.5% of the photons (< 300 nm) irradiated into the catalyst bed if the reaction required one photon to produce one molecule of methanal. Both UV irradiation and reaction temperatures as high as 500 K were indispensable. These molybdenum oxide catalysts were more effective for the photooxidation of ethane and propane to give aldehydes and ketones in high yields (*ca.* 80 μmol h^{-1}). According to XPS, UV diffuse reflectance and XRD studies, the active species seems to be the coordinatively unsaturated M=O species in the terminal position of less dispersed molybdenum species, but not from large crystallites of MoO_3.

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