Photo-oxidation of light alkenes using solid metal oxide semiconductor-based catalysts: Effects of reaction temperature and metal oxide additives

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The photo-oxidation of ethene and propene using zinc oxide and titanium oxide-based catalysts has been investigated at various reaction temperatures. The activity of the zinc oxide catalyst (0.25 g) was greatly enhanced when the reaction temperature was raised to 450–500 K, to afford 21 μmol h^{-1} of ethanal, 16 μmol h^{-1} of propenal and 49 μmol h^{-1} of carbon oxides, together with small amounts of propanal and methanal at 493 K. Loading of Group 5 or 6 metal oxide species on zinc oxide suppressed the formation of carbon oxides and propenal, whereas a significant formation of propanal was observed in addition to ethanal. Molybdenum oxide-loaded catalysts showed high selectivities toward oxygen-containing chemicals. Since the MoO_3/SiO_2 catalyst showed a similar product distribution in the photo-oxidation of propene, surface active centres including molybdenum species on zinc oxide surface seem to be responsible for the reaction. The use of titanium oxide-based catalysts at ambient temperature generally resulted in low selectivities toward oxygen-containing chemicals.

Studies on the photo-assisted catalytic reaction of alkenes such as propene using solid oxide catalysts that span the range from those including discrete molecules[1–10] to solid oxide semiconductors[11] have been performed. Most of the studies using the highly dispersed supported oxide catalysts focused on the details of the reaction mechanisms. Anpo *et al.* have investigated photo-isomerization and photo-induced metathesis of alkenes using highly dispersed supported transition-metal oxide catalysts such as V_2O_5/PVG (porous Vycor glass), MoO_3/PVG and MoO_3/SiO_2.[1–5] Formation of the intermediate bridge-type π-complex by the reaction of the alkene and the O^- site on the charge-transfer excited triplet species was proposed on the basis of photoluminescence spectroscopy. Photo-oxidation of alkenes with molecular oxygen using supported vanadium and niobium oxide catalysts has been investigated extensively by Yoshida and co-workers[6–10] The selective formation of ethanal, propanal and propenal from propene, or ethanal from ethene were reported. Propanal was formed with the reaction of but-1-ene, while ethanal was predominantly formed from but-2-ene. They proposed a one-to-one intermediate complex comprising of one molecule of alkene and one molecule of oxygen on the basis of a kinetic study[7] and *ab initio* Hartree–Fock molecular orbital calculations.[10] On the other hand, photo-oxidation of propene using solid oxide semiconductors such as TiO_2 has been investigated by Pichat *et al.*[11] They found that TiO_2 showed the highest catalytic activity, but the main product was carbon dioxide even at low conversion level. Zinc oxide was reported to show a significantly lower activity than that of TiO_2 at room temperature. These authors also reported that increasing the temperature to 455 K decreased the activity of TiO_2.

In previous papers, we have described selective photo-assisted catalytic oxidation of light alkanes, including methane, on the MoO_3/SiO_2[12–14], V_2O_5/SiO_2,[15] and ZnO-based catalysts.[16,17] An elevated reaction temperature as high as *ca.* 500 K enhanced the activities of these catalysts. We also found that addition of molybdenum species on zinc oxide markedly improved the selectivity for methanal in the photo-oxidation of methane, whereas pure zinc oxide mainly afforded carbon dioxide.[16] The detailed roles of the molybdenum species on the surface, however, have not yet been clarified.

The present study focuses on the photo-assisted catalytic oxidation of propene and ethene using zinc oxide-based catalysts. Effects of reaction temperature and additives loaded onto the zinc oxide surface on the product distribution are described. Plausible reaction mechanisms, roles of additives, and the nature of active centres on the surface are also discussed.

Experimental

Materials

Zinc oxide (Wako, 99.9%, BET surface area 4.7 m^2 g^{-1}, particle size 0.3 μm, packing density 0.7 g cm^{-3}) was used as received. Two kinds of titanium oxide were also used, one in anatase form delivered from Wako (BET surface area 8.5 m^2 g^{-1}, particle size 0.15 μm) and the other JRC-TIO-1 (mostly anatase, BET surface area 76.2 $m^2 g^{-1}$, including 3.63% of SO_3) acquired from the Catalysis Society of Japan. Loaded catalysts were prepared by the usual impregnation method from an aqueous solution of ammonium salts, *i.e.* ammonium heptamolybdate or ammonium metavanadate. We also prepared a 'water-treated' zinc oxide catalyst, further designated as ZnO-W, which was prepared as follows. Zinc oxide was immersed in distilled water for 1 day, followed by drying and calcination at 823 K in a stream of dried air for 2 h (packing density 1.1 g cm^{-3}, particle size was unchanged). The 'water-treated' catalyst was used for the precise discussion on effects of additives, since metal oxide loaded zinc oxide catalysts exhibited smaller packing densities than parent zinc oxide, and those similar to ZnO-W. The MoO_3/SiO_2 catalyst was prepared by the usual pore volume impregnation method using silica gel (Alfa, surface area 300 m^2 g^{-1}).

Gaseous reactants, propene, oxygen and helium, were used as received without any further purification. Tetrahydrofuran and other organic liquid reagents were distilled before use.

Apparatus and procedures

The catalyst (0.25 g) was activated in dry, carbon dioxide-free air (20 cm^3 min^{-1}) at 823 K for 2 h *in situ* just before the reaction. An upstream flow fixed-bed reactor made of silica glass was used for the reaction. The catalyst was mounted in a flat cell (10 mm × 20 mm, inner thickness 1.5 mm), and covered by another silica glass tube (35 mm id). The temperature of the catalyst bed was maintained by passing heated air around the flat cell, and was monitored by a thermocouple directly inserted into the catalyst bed.[17] The area of the window for UV irradiation was a function of the packing densities of the catalysts: 2.4 cm^2, 1.5 cm^2, 1.5 cm^2 for 0.25 g of pure zinc oxide, ZnO-W and the loaded zinc oxide catalysts, respectively. The sizes of window for JRC-TIO-1 and TiO_2 (Wako, anatase) were 2.1 cm^2 and 2.7 cm^2. UV irradiation was carried out using a high-pressure mercury vapour lamp (200 W, arc length 75 mm) with a water filter. The number of photons irradiated into the catalyst bed measured by chemical actinometry using iron(III) ammonium oxalate for 250–500 nm varied in proportion to the area of window, *i.e.* 1.6×10^{-6} einstein s^{-1} for pure zinc oxide and 1.0×10^{-6} einstein s^{-1} for ZnO-W and the loaded zinc oxide catalysts. The reaction was typically carried out under the following conditions: alkene feed rate, 7.5 mmol h^{-1}; molar ratio alkene : O_2 : He = 3 : 1 : 10; W/F (weight of the catalyst divided by the total feed of the reaction gas), 7.1 g h mol^{-1}; catalyst bed temperature, 493 K. Liquid products were collected into a trap containing tetrahydrofuran at 195 K, and gaseous products were collected into gas-sampling bags.

Analysis

Products were analysed by gas chromatography using a Porapak-N column at 433 K with FID for ethanal, propene oxide and acetone; a Gaskuropak 54 column at 413 K with FID for propenal and propanal; a TSG-1 on Shimarite-F column at 393 K with TCD for methanal. Gaseous products were analysed using a Porapak-Q column at 353 K with FID for C_1–C_4 hydrocarbons, a molecular sieve 5A column at 323 K with TCD for oxygen, and an active carbon column at 323 K with TCD for H_2, CO and CO_2 (detection limit: carbon oxides <20 ppm; aldehydes and alcohols *ca.* 0.1 μmol).

Atomic absorption analysis was carried out to determine the loading levels of additives using an AA-8200 atomic absorption/flame emission spectrometer (Nippon Jarrell Ash Inc.). UV–VIS diffuse reflectance spectra were measured using a Shimadzu model MPS-2000 multipurpose spectrophotometer equipped with an integrating sphere (50 mm id). Magnesium oxide (Wako) was used as a reflectance standard. An X-ray diffraction study was performed using a Rigaku Geigerflex with Cu-Kα emission in the range $5 < 2\theta$/degrees < 70. X-Ray photoelectron spectra (XPS) of the molybdenum-loaded zinc oxide catalysts were recorded with a Perkin Elmer 5500 MT system using Al-$K\alpha_{1,2}$ radiation (15 kV, 400 W) operated at room temperature, under a pressure of $<1 \times 10^{-8}$ Torr. The electron take-off angle was set at 45°. The spectral accumulation time was *ca.* 40 min for Mo 3d and 10 min Zn $3p_3$ lines of the MO_3/ZnO catalysts. The binding energies were referenced to the C 1s level. The extent of the dispersion of supported molybdenum species was estimated on the basis of the measurements in terms of relative peak-area intensities of Mo $3d_{5/2}$ (232.7 eV), Mo $3d_{3/2}$ (235.9 eV), Mo $3p_3$ (398.2 eV), Zn $2p_3$ (1021 eV), O (1s) 531.1 eV) and C 1s (284.6 eV), where the atomic sensitivity ratio of Mo 3d/Zn $2p_3$ = 0.891.

The BET surface areas of the catalysts were measured by the use of a Belsorp 28 from BEL Japan Inc., a microprocessor-controlled automatic system using molecular nitrogen. The apparent shape and size of the catalyst particles were observed with Jeol JSM-T100 and Hitachi S-2500CX scanning electron microscopes (SEM).

Results and Discussion

The yields in the tables and figures were calculated from the amounts of products in the effluent gases per unit time. A small amount of carbon dioxide (<0.5 μmol) was evolved by heating the zinc oxide-based catalysts to 823 K under argon just after the completion of the reactions.

Photo-oxidation of propene using zinc oxide-based catalysts

Table 1 shows the results of photo-oxidation of propene using the zinc oxide-based catalysts during the first 1 h at 493 K. The reaction using pure zinc oxide afforded ethanal, propenal and carbon oxides together with small amounts of propanal, acetone and methanal. No carboxylic acid could be detected by GC analysis. One-pass conversion of propene was estimated to be 50 μmol h^{-1} (0.7% of propene feed) with a selectivity of 67% for the oxygen-containing chemicals, whereas

Table 1 Photo-oxidation of propene using the zinc oxide-based catalysts at 493 K[a]

		yields/μmol h^{-1}						
run	catalyst[b]	propenal	propanal	acetone	ethanal	methanal	CO	CO_2
1	ZnO	16	trace	1.4	21	5	10	39
2[c]	ZnO	nd	nd	nd	nd	nd	nd	nd
3[d]	ZnO	nd	nd	nd	nd	nd	trace	4
4[e]	ZnO	1.3	0.2	0.1	0.2	—	nd	trace
5	ZnO-W	7.2	0.7	0.3	10	1	4	18
6	Li_2O/ZnO	6.4	0.2	1.4	14	—	9	59
7	Na_2O/ZnO	6.4	0.6	0.6	11	—	5	39
8	K_2O/ZnO	2.5	0.1	0.7	13	—	8	58
9	V_2O_5/ZnO	1.5	1.2	0.8	7.7	—	trace	5
10	Cr_2O_3/ZnO	3.7	0.2	0.2	3.1	—	1	17
11	MoO_3/ZnO	2.3	2.5	0.6	15	3	1	8
12[c]	MoO_3/ZnO	nd	nd	nd	nd	nd	nd	nd
13	MoO_3/ZnO[f]	3.9	2.2	0.7	14	—	trace	16
14	WO_3/ZnO	1.3	trace	trace	5.3	—	trace	3
15	RuO_2/ZnO	2.7	nd	0.3	1.9	—	1	9
16[g]	MoO_3/SiO_2	7.1	2.3	0.9	5.3	2	1	4
17[g,h]		nd	nd	nd	1.8	nd	nd	trace
18[c,g]		nd	nd	nd	nd	nd	nd	nd
19[g]	V_2O_5/SiO_2	11	4.3	1.4	13	—	2	4

[a] Amount of catalyst 0.25 g, propene feed rate 7.5 mmol h^{-1}; C_3H_6 : O_2 : He = 3 : 1 : 10, W/F = 7.1 g h mol^{-1}; nd, not detected; —, not determined, 1 h. [b] Loading level 1.0 wt.% in prepration (actually, 0.8 wt.% for calcined MoO_3/ZnO). [c] Without UV irradiation at 501 K. [d] Without UV irradiation at 573 K. [e] Without molecular oxygen, C_3H_6 : He = 3 : 11. [f] Mechanically mixed, loading level 0.3 wt.%. [g] Amount of catalyst 0.025 g; W/F = 0.71 g h mol^{-1}; fluidized catalyst bed; loading level = 2.5 wt.% in preparation. [h] Temperature = 335 K.

Pichat *et al.* have reported that the reaction at 320 K using ZnO gave aldehydes and acetone at the lower selectivity of 22–53% even at low conversion levels (0.055%).[11] The contribution of the thermal oxidation of propene could be excluded, because none of the products was observed in the absence of UV irradiation at 501 K (run 2). The 'water-treated' zinc oxide catalyst (ZnO-W) of higher apparent packing density afforded products in lower yields than the parent zinc oxide, probably owing to its lower apparent irradiation area (run 5).

Fig. 1(*a*) shows the effects of the reaction temperature using ZnO. While very small amounts of oxidation products were observed at an ambient temperature of 336 K, the photoconversion of propene was improved by raising the reaction temperature. The oxygen-containing chemicals such as ethanal and propenal were formed in the high yields at 493 K. Further increase in the reaction temperature decreased the yields of aldehydes, whereas the formation of carbon oxides were enhanced. Secondary oxidation of the products of intermediates to carbon oxides might be enhanced at such a high temperature.

The effects of various additives on zinc oxide were examined at 493 K, and the results are listed in Table 1 (the loaded catalysts are further designated as MoO_3/ZnO irrespective of the real form of the additives). Their surface acid–base properties affect the stability of intermediates and the secondary reaction. In general, the catalysts with basic additives seem to enhance deep oxidation. Loading of an alkali-metal oxide, such as Li_2O, Na_2O or K_2O, enhanced the activity, and the yield of ethanal and carbon dioxide increased (*vs.* ZnO-W). On the other hand, the impregnation of molybdenum species on zinc oxide changed the product distribution significantly (run 11). A small amount of propanal (2.5 μmol h^{-1}) was formed, which was detected only in a trace amount with the zinc oxide catalyst. The yield of propenal markedly decreased from 7.2 to 2.3 μmol h^{-1} with loading of molybdenum species, and the formation of carbon oxides was greatly suppressed, implying the improved selectivity for oxygen-containing chemicals. It should be noted that addition of MoO_3 (crystalline size *ca.* 5 μm) by mechanical mixing induced similar changes in the product distribution, although the yield of carbon dioxide was relatively high, 16 μmol h^{-1} (run 13). As shown in a later section, zinc oxide was very sensitive to additives, and a very small amount of molybdenum species (<0.2 wt.% as MoO_3) could significantly change the catalytic properties. With a mechanically mixed catalyst, migration of molybdenum species onto zinc oxide surface would occur during the calcination at 823 K, because of the volatility of molybdenum oxide at such a high temperature,[1] and this would markedly change the catalytic activity. The relatively high yield of carbon dioxide would be due to the presence of Mo-uncovered zinc oxide surface.

Fig. 1(*b*) shows the effects of reaction temperature using MoO_3 (0.8 wt.%)/ZnO catalyst. The results clearly indicate that elevated temperatures as high as 500 K are indispensable for the photo-conversion of propene. It should be noted that at temperatures above 500 K, the yield of propanal markedly increased, whereas the yields of ethanal and carbon dioxide decreased.

Fig. 2 shows the effect of *W*/*F* on the yields of the products by changing the amount of the zinc oxide and MoO_3 (0.8 wt.%)/ZnO catalysts. The conversion of propene and all the product yields increased linearly with increasing *W*/*F*. On the other hand, the selectivities were not affected by changing *W*/*F*. These results suggest that most of the products including carbon oxides were not formed by the secondary oxidation of the primary products.

Fig. 3 illustrates the effects of the loading level of molybdenum species on the photo-oxidation yields of propene at 493 K. At *ca.* 0.1–0.2 wt.% of MoO_3 loading the yield of ethanal was a maximum. Decreases in the yields of carbon dioxide and propenal, and the formation of propanal were also observed. With a loading level higher than 0.2 wt.%, the constant yields and the selectivities of the products were observed.

Fig. 4 plots the XPS intensity ratio *I*(Mo 3d)/*I*(Zn $2p_3$) as a function of the total atomic ratio N_{Mo}/N_{Zn}, where *I*(Mo 3d) and *I*(Zn $2p_3$) represent the XPS peak intensities, and N_{Mo} and N_{Zn} are the numbers of atoms. The values of *I*(Mo 3d)/*I*(Zn $2p_3$) and N_{Mo}/N_{Zn} were in direct ratio within *ca.* 0.1 wt.% of the loading level of MoO_3. With a loading higher than 0.1 wt.%, the value of *I*(Mo 3d)/*I*(Zn $2p_3$) became lower than

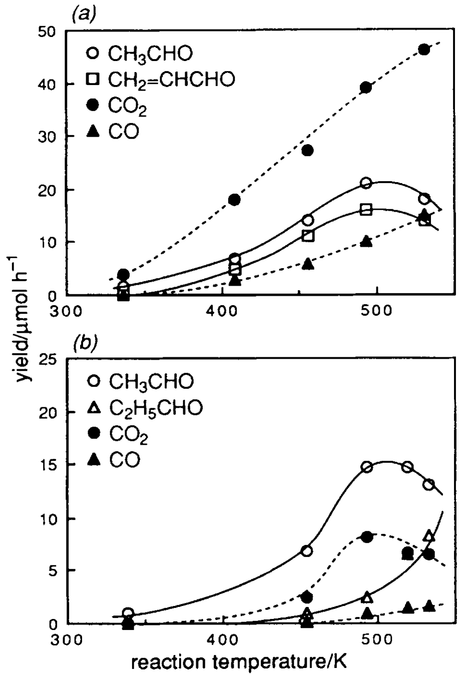


Fig. 1 Photo-oxidation of propene using (*a*) the ZnO catalyst and (*b*) the MoO_3 (0.8 wt.%)/ZnO catalyst at various reaction temperatures. Amount of catalyst, 0.25 g; propene feed rate, 7.5 mmol h^{-1}; $C_3H_6 : O_2 : He = 3 : 1 : 10$; $W/F = 7.1$ g h mol^{-1}.

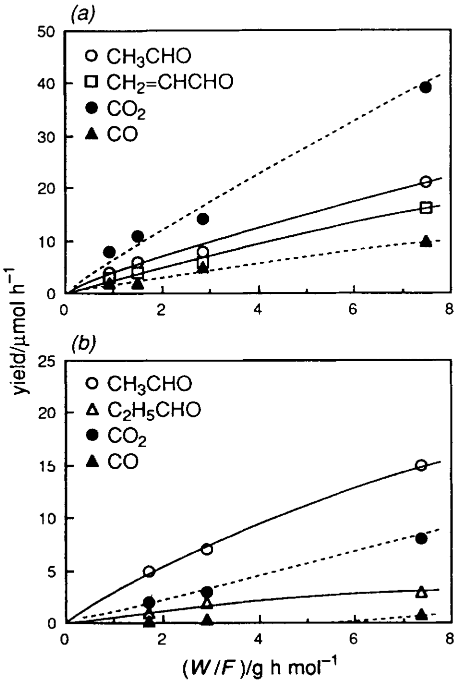


Fig. 2 Effects of *W*/*F* by changing the amount of (*a*) the ZnO catalyst and (*b*) the MoO_3 (0.8 wt.%)/ZnO catalyst. Reaction-gas composition was the same as in Fig. 1.

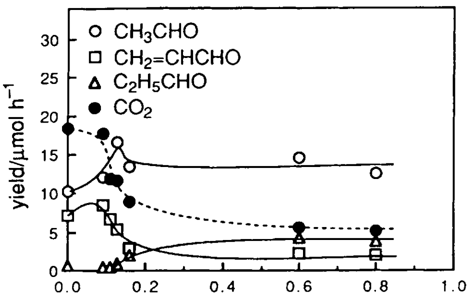


Fig. 3 Effects of loading level of MoO_3 on ZnO. Amount of catalyst, 0.25 g; reaction-gas composition was the same as shown in Fig. 1.

expected. This result indicates that molybdenum species dispersed well on the surface of zinc oxide within a loading level of *ca.* 0.1 wt.%. A further increase in loading level, however, would induce the formation of multilayers of molybdenum species, probably an α-$ZnMoO_4$-like phase (see below). Therefore the dramatic changes in the product yields of photo-oxidation of propene obtained in the range 0.1–0.2 wt.% might be due to the well dispersed molybdenum multilayers.

The XRD study of molybdena-loaded zinc oxide at various loading levels was carried out. The catalyst with 5 wt.% MoO_3 loading showed small peaks attributed to α-$ZnMoO_4$ [$d = 0.365$ nm (201), 0.341 nm ($\bar{1}20$), 0.335 nm ($\bar{2}02$), relative intensity; 2(α-$ZnMoO_4$ $\bar{2}02$)/100(Zn 111)] in addition to those of crystalline zinc oxide. No other peaks such as those of MoO_3 were observed. The peaks of α-$ZnMoO_4$ almost disappeared for the catalyst with loading <0.8 wt.%. The UV–VIS diffuse reflectance spectra of pure zinc oxide and the Mo-loaded catalysts (up to 5 wt.% as MoO_3) were almost identical. They showed a red limit at *ca.* 380 nm.

We also examined the photo-oxidation of propene using the silica-supported MoO_3 or V_2O_5 catalysts (runs 14–17 in Table 1); these have been found to show excellent catalytic activities for the photo-oxidation of light alkanes at elevated temperatures.[12–15] It should be noted that the product distribution using MoO_3/SiO_2 was quite similar to that for the MoO_3 (0.8 wt.%)/ZnO catalyst. A considerable amount of propanal (2.3–4.3 µmol h^{-1}) was formed in addition to ethanal and propenal using MoO_3/SiO_2 or V_2O_5/SiO_2, suggesting that the formation of propanal is a characteristic feature of the Mo- or V-loaded catalysts.

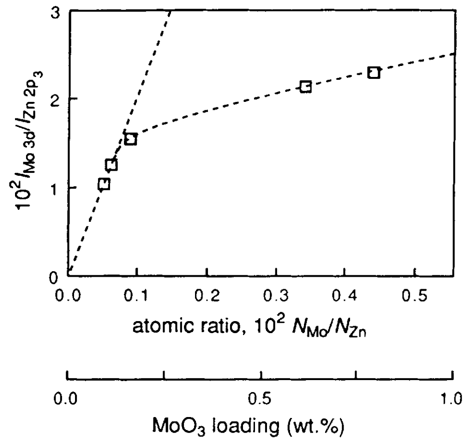


Fig. 4 XPS intensity ratio I(Mo 3d)/I(Zn $2p_3$) as a function of overall atomic ratio of Mo and Zn of the MoO_3/ZnO catalysts

In order to examine whether the photo-activation of additives directly participated in the reaction or not, the effects of cut-off filters were investigated. As shown in Table 2, with the ZnO catalyst, the use of a Pyrex filter (passes >300 nm) cut down all the yields of the products except for propanal by *ca.* 40%. With the MoO_3/ZnO catalyst, the yields similarly decreased with a Pyrex filter, whereas the yield of propanal was almost constant. With the UV-35 filter (passes >350 nm; transmittance at 330 nm, 10%), the reaction also takes place, although the yields of the products decrease. These results suggest that zinc oxide and molybdenum oxide-loaded catalysts have a similar dependence on irradiation wavelength.

Photo-oxidation of propene using titanium oxide-based catalysts

The results of photo-oxidation of propene using several titanium oxide catalysts for 1 h are shown in Table 3. Without heating the catalyst bed, at 338 K, the JRC-TIO-1 catalyst mainly afforded ethanal and carbon dioxide. Acetone was predominant among C_3-products. It should be noted that propan-2-ol, the product of propene hydration, was observed, probably due to the surface acidity induced by SO_3 contaminant (see Experimental). The reagent-grade anatase showed lower activity, but similar selectivity to JRC-TIO-1. At 337 K, the reaction without UV irradiation only gave a small amount of propan-2-ol, the hydrated product. These results indicate quite different selectivity of TiO_2 from the zinc oxide catalyst, although many factors, especially particle size, would effect the efficiency of the catalyst. In general, the smaller particle size and therefore larger specific surface area are favourable to show significant activity for solid oxide semiconductor photocatalysts,[17] but such changes did not significantly affect the intrinsic selectivity of the titanium oxide catalysts.

Fig. 5 shows the effects of reaction temperature on photo-assisted and thermal catalytic reactions of propene using JRC-TIO-1. The titanium oxide catalysts showed quite different behaviour with regard to reaction temperature from the zinc oxide-based catalysts. As shown in (*a*), the yields of the products gradually decreased with increasing reaction temperature from *ca.* 330 to *ca.* 440 K, being consistent with the results by Pichat *et al.*[11] At higher reaction temperatures, large amounts of carbon monoxide and carbon dioxide were formed. But as shown in Fig. 5(*b*), almost equal amounts of carbon oxides were produced without UV irradiation, indicating the predominance of thermal catalytic oxidation above 440 K.

The effects of molybdenum oxide loading on JRC-TIO-1 were examined, but the selectivities for the desired products

Table 2 Effects of cut-off filters on photo-oxidation of propene using the zinc oxide-based catalysts at 493 K[a]

			yields/µmol h^{-1}						
run	catalyst	filter	propenal	propanal	acetone	ethanal	methanal	CO	CO_2
1	ZnO	no	16	trace	1.4	21	5	10	39
2	ZnO	Pyrex	8.6	0.4	0.6	12	1	7	23
3	MoO_3/ZnO[b]	no	2.3	2.5	0.6	15	3	1	8
4	MoO_3/ZnO[b]	Pyrex	1.5	2.6	0.5	9.2	2	trace	5
5	MoO_3/ZnO[b]	UV-35	0.6	0.5	trace	1.2	—	nd	trace

[a] Amount of catalyst 0.25 g; propene feed rate = 7.5 mmol h^{-1}, $C_3H_6 : O_2 : He = 3 : 1 : 10$; $W/F = 7.1$ g h mol^{-1}; nd, not detected; —, not determined, 1 h. [b] Loading level 0.8 wt.% after calcination.

Table 3 Photo-oxidation of propene using the titanium oxide-based catalysts[a]

			yields/μmol h^{-1}						
run	catalyst	T/K	propenal	propanal	acetone	propan-2-ol	ethanal	CO	CO_2
1	TiO_2(JRC-TIO-1)	338	0.6	0.4	2.8	3.2	20	3	32
2	TiO_2 (anatasa)	326	0.6	nd	1.0	nd	5.3	trace	14
3[b]		337	nd	nd	nd	3.9	nd	nd	nd
4	MoO_3 (1.1 wt.%)/TiO_2(JRC-TIO-1)	338	0.2	0.2	1.0	3.3	12	1	13
5[b]		336	nd	nd	nd	3.2	nd	nd	nd
6		493	nd	0.3	11	8.5	5.5	32	42
7[b]		493	nd	nd	12	29	4.1	32	42

[a] Amount of catalyst 0.25 g; propene feed rate 7.5 mmol h^{-1}; $C_3H_6 : O_2 : He = 3 : 1 : 10$; $W/F = 7.1$ g h mol^{-1}; nd, not detected, 1 h. [b] Without UV irradiation at 501 K.

were still low (runs 4–7 in Table 3). Fig. 6 shows effects of loading levels on the yields of major products at around 388 K, indicating that the selectivity toward oxygen-containing chemicals, *i.e.* ethanal, gradually improved with increasing loading level. But the yield of ethanal markedly decreased with molybdenum oxide over 0.2 wt.%.

Photo-oxidation of ethene

The results of the photo-oxidation of ethene at 493 K are listed in Table 4. With zinc oxide small amounts of methanal and ethanal were formed, together with a large amount of carbon oxides, 58 μmol h^{-1}. The reaction without UV irradiation over zinc oxide gave no products. With titanium oxide catalysts, deep oxidation was predominant. On the other hand, the reaction using the MoO_3 (0.8 wt.%)/ZnO catalyst gave 7 μmol h^{-1} of methanal and 1.5 μmol h^{-1} of ethanal together with small amounts of carbon oxides. The addition of molybdenum oxide onto zinc oxide suppressed oxidation, and enhanced partial oxidation.

Possible reaction mechanisms and roles of additives

Since propene oxide was supposed to be an intermediate of oxygen-containing compounds on photo-oxidation of propene, the reaction of propene oxide was examined (Table 5). The reaction over both the ZnO and MoO_3/ZnO catalysts gave propanal selectively. With the titanium oxide catalyst at 344 K, propanal was still the main product, although formation of acetone and ethanal was observed. The reaction using these catalysts without UV irradiation also selectively gave propanal. These results suggest that if the propene oxide-like intermediate is formed, propanal should be produced selectively using both the pure and loaded catalysts even in the absence of light. With the MoO_3/ZnO catalyst, propanal would be produced *via* a propene oxide-like intermediate. However, formation of a very small amount of propanal from propene was observed using pure zinc oxide and titanium oxide (see Tables 1 and 3). These results indicate that significant formation of a propene oxide-like intermediate during the photo-oxidation of propene using these pure oxides can be

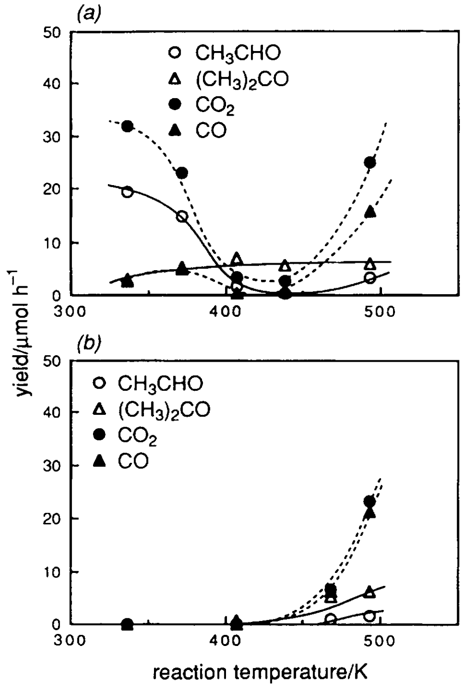


Fig. 5 (*a*) Photo-assisted and (*b*) thermal catalytic oxidation of propene using a TiO_2(JRC-TIO-1) catalyst at various reaction temperatures. Amount of catalyst, 0.25 g; reaction-gas composition was the same as in Fig. 1.

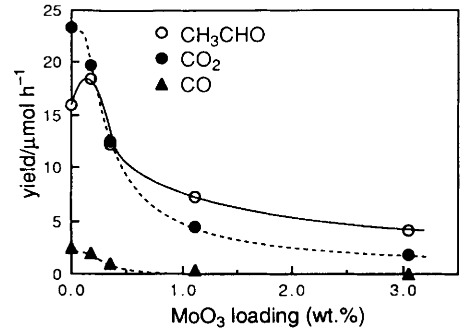


Fig. 6 Effects of loading level of MoO_3 on TiO_2 (JRC-TIO-1) at *ca.* 340 K. Amount of catalyst, 0.25 g; reaction-gas composition was as shown in Fig. 1.

Table 4 Photo-oxidation of ethene using various solid oxide semiconductor-based catalysts[a]

			yields/μmol h^{-1}					
run	catalyst	T/K	ethanal	EO[b]	ethanol	methanal	CO	CO_2
1	ZnO	493	0.9	nd	nd	trace	17	41
2[c]	ZnO	493	nd	nd	nd	nd	nd	nd
3	MoO_3/ZnO[d]	493	1.5	nd	nd	7	1	6
4	TiO_2 (JRC-TIO-1)	341	0.7	trace	nd	3	7	26
5	TiO_2 (anatase)	335	trace	nd	nd	trace	trace	19

[a] Amount of catalyst 0.25 g; ethene feed rate = 7.5 mmol h^{-1}; $C_2H_4 : O_2 : He = 3 : 1 : 10$; $W/F = 7.1$ g h mol^{-1}; nd not detected, 1 h. [b] EO = Ethene oxide. [c] Without UV irradiation. [d] Loading level 0.8 wt.% after calcination.

Table 5 Photo-assisted or thermal catalytic reaction of propene oxide using various solid oxide semiconductor-based catalysts[a]

				selectivity (%)					
run	catalyst	T/K	conf. (%)	propenal	propanal	acetone	ethanal	CO	CO_2
1	ZnO	493	3.3	0	79	0	9	3	9
2[b]	ZnO	493	0.6	0	93	0	0	0	7
3	MoO_3/ZnO[c]	493	1.5	0	96	2	0	0	2
4	TiO_2 (JRC-TIO-1)	344	1.5	0	48	22	28	0	2
5[b]	TiO_2 (JRC-TIO-1)	348	0.8	0	100	0	0	0	0

[a] Amount of catalyst 0.25 g; C_3H_6O feed rate 7.5 mmol h^{-1}; $C_3H_6O : O_2 : He = 3 : 1 : 10$; $W/F = 7.1$ g h mol^{-1}, 1 h. [b] Without UV irradiation. [c] Loading level 0.5 wt.% in preparation.

excluded, although Pichat *et al.*[11] proposed the possibility of a propene oxide-like intermediate on TiO_2.

Photo-assisted and thermal catalytic activities of zinc oxide toward oxidation of carbon monoxide,[18] decomposition of N_2O,[19,20] and the oxygen-exchange reaction[21] have been investigated extensively by Tanaka *et al.* They demonstrated the participation of O^- anion radical species in the photo-oxidation of carbon monoxide at *ca.* 470 K. A lattice oxygen of zinc oxide, $O_{lattice}{}^{2-}$, trapped the positive hole produced by UV irradiation [eqn. (1)], forming $O_{lattice}{}^{-}$ species [eqn. (2)].

$$ZnO \xrightarrow{h\nu} h^+ + e^- \qquad (1)$$

$$O_{lattice}{}^{2-} + h^+ \longrightarrow O_{lattice}{}^{-} \qquad (2)$$

The $O_{lattice}{}^{-}$ species might react with alkenes to give aldehyde selectively, since the reaction without molecular oxygen produced small amounts of oxygen-containing chemicals and none of the carbon oxides (see run 3 in Table 1). On the other hand, since $O_3{}^-$ species, produced by the reaction between the $O_{lattice}{}^{-}$ and molecular oxygen [eqn. (3)], was proposed to be an intermediate of the oxygen-exchange reaction[21] and detected by EPR at 77 K,[22] participation of such active oxygen species derived from adsorbed molecular oxygen cannot be ruled out. Another important role of molecular oxygen would be the re-oxidation of the reduced surface of the zinc oxide catalyst [eqn. (4)].

$$O_{lattice}{}^{-} + O_2 \rightarrow O_3{}^{-} \qquad (3)$$

$$O_2 + e^- \rightarrow O_{2\,ads}{}^{-} \qquad (4)$$

$$\rightarrow \rightarrow 2O_{lattice}{}^{2-}$$

On the surface of the titanium oxide catalyst, intervention of another active oxygen species, *i.e.* O, has also been proposed.[11,23,24] The O species was assumed to be formed by the recombination of a photo-produced electron and the positive hole [eqn. (5) and (6)][23] or other pathways.[24]

$$O_3{}^{-} + e^- \rightarrow 2O + O_{lattice}{}^{2-} \qquad (5)$$

$$O_{2\,ads}{}^{-} + h^+ \rightarrow 2O \qquad (6)$$

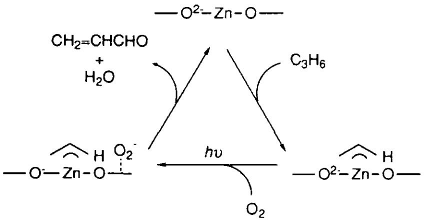
Elevated reaction temperature would promote the desorption of the oxygenated products from the surface and re-oxidation of the reduced surface to increase the turnover frequency, provided that photo-generated active oxygen species were sufficiently stable.[17] Since the type and thermal stability of surface oxygen species seem to be responsible for the differences in the selectivity and temperature dependence between zinc oxide catalysts and titanium oxide-based catalysis, details of the properties of the active oxygen species are now under investigation.

One of the probable mechanisms for the photo-oxidation of alkenes on zinc oxide is shown in Scheme 1. Dent and Kokes[25,26] reported the formation of stable surface π-allyl species by chemical adsorption of propene onto zinc oxide in the dark. In the present study, the active oxygen species would abstract hydrogen from the terminal carbon of π-allylic species coordinated onto surface zinc to produce mainly case of the photo-oxidation of ethene, which does not have a reactive allylic C—H bond, complicated reactions would occur to form carbon oxides.

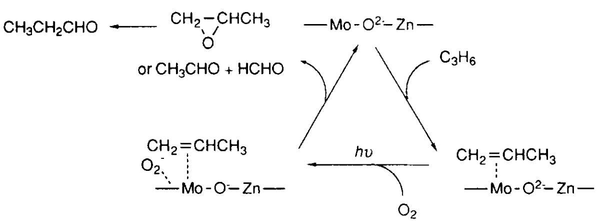
The catalytic activity and selectivity of the parent zinc oxide were markedly altered by the addition of Group 5 or 6 metal oxide, especially MoO_3 or V_2O_5. The reaction mechanisms of the photo-oxidation of silica-supported Group 5 and 6 metal oxide catalysts have been investigated extensively by Yoshida and co-workers,[6–10] and the reaction was reported to be initiated by photo-excitation of surface M═O double bond species to form a charge-transfer complex. Then, interaction of the alkene, molecular oxygen and excited surface species would form the one-to-one intermediate complex. Note that photo-excitation of MoO_3/SiO_2 required irradiation shorter than 300 nm. UV diffuse reflectance studies have revealed that MoO_3 (2.5 wt.%)/SiO_2 shows no significant absorption bands above 300 nm.[12,14] On the other hand, in the present study the photo-oxidation of propene on MoO_3/ZnO was not essentially suppressed by cutting off UV irradiation of a wavelength shorter than 300 nm, and the product distribution was almost unchanged (see Table 2). Therefore the reaction seems not to be initiated with the direct photoactivation of surface Mo═O species (if present), but with the activation of zinc oxide support (red limit *ca.* 380 nm).

The plausible roles of Group 5 or 6 metal oxide additives are as follows. One might be to suppress the activity of the catalyst. Both physical coverage of the active sites of zinc oxide, and promotion of the re-combination of positive holes and electrons were supposed to be one of the reasons for lower activity. In addition, the results in the present study reveal that predominant formation of ethanal and propanal rather than allylic oxidation are characteristic features for the Mo- or V-loaded ZnO catalysts. Since similar product distribution was observed on photo-oxidation of propene over the silica-supported MoO_3 catalyst, we may estimate that similar types of intermediate were formed on the surfaces of MoO_3/ZnO and MoO_3/SiO_2.

On the other hand, Tanaka and Blyholder have demonstrated that, in contrast to the case with zinc oxide, π-coordination of alkenes was predominant with some transition-metal oxides, *i.e.* Co_3O_4.[27] In addition, Yoshida and co-workers proposed the propene oxide-like intermediate in the photo-oxidation of propene using MoO_3/SiO_2.[8] The present results and precedent studies lead us to the idea illustrated in Scheme 2. Propene is adsorbed onto surface molybdenum species in π-coordination, while active oxygen species is formed on the ZnO surface. The interaction between coordinated propene and active oxygen species would form an



Scheme 1



Scheme 2

mediate to form propanal. Ethanal would also be formed from such intermediate *via* ozonide-type double-bond fission. The reaction with ethene would proceed *via* epoxide-like intermediates for ethanal and double-bond fission for methanal.

Conclusions

Photo-assisted catalytic activities of the zinc oxide catalyst toward the oxidation of propene and ethene were enhanced at a temperature as high as 500 K. Propenal, ethanal and carbon dioxide were predominantly formed over zinc oxide, whereas the reaction with ethene mainly produced carbon oxides. On the other hand, addition of molybdenum or vanadium species onto zinc oxide induced the formation of propanal in addition to ethanal, and greatly suppressed the formation of propenal and carbon dioxide from propene, implying improved selectivity for oxygen-containing chemicals. The reaction with ethene mainly produced methanal. On the MoO_3/ZnO catalysts, the interaction between π-coordinated propene and active oxygen species would induce an epoxide-like intermediate to form mainly propanal and double-bond fission for ethanal formation from propene. The titanium oxide-based catalysts mainly afforded carbon dioxide at an ambient temperature both from ethene and propene, and showed a completely different temperature dependence from those of the zinc oxide-based catalysts.

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