Catalytic Activity of Sn-Mo Oxides for Propene Oxidation

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Sn–Mo oxides were subjected to experimental studies with reference to their catalytic C_3H_6 oxidation and their own reduction by C_3H_6. In the oxidation Sn–Mo oxides are 30—40 times more active than MoO_3 but only 4—5 times than SnO_2. With Sn–Mo oxides as well as SnO_2, the oxidation is zero order in C_3H_6 and about half order in O_2, in contrast to those with MoO_3. It is proposed that the oxidation proceeds via a redox mechanism with the reduction step proceeding very rapidly. ^{18}O tracer experiments show that the mobility of lattice oxygen in Sn–Mo oxides is lower than that in MoO_3 but similar to that in SnO_2. From these results together with those of structural studies, it is concluded that the active phase of Sn–Mo oxides is characterized by the MoO_3 highly dispersed on SnO_2 or Mo ions dissolved in SnO_2, and that their high reducibility possibly originates from the existence of SnO_2 itself in them.

Partial oxidation of alcohols on Sn-Mo oxides has been investigated by several workers, *e.g.*, Niwa *et al.*[1] and Okamoto *et al.*,[2] who investigated the mechanism of the oxidation and the correlation between activity and surface structure for these systems, respectively, by using various techniques such as ESR and XPS. As regards the oxidation of alkenes on Sn–Mo oxides, Morooka *et al.*,[3] Butein,[4] and Ai[5] investigated oxidation at lower temperatures in the presence of water vapor and emphasized the importance of acid-base properties of the oxides in the oxidation. Although the alkene oxidation at higher temperatures has been invesigated by several workers,[6,7] no detailed kinetic studies on the oxidation have been reported. Margolis[6] investigated the propene oxidation by Mössbauer spectroscopy and concluded that adsorbed oxygen plays a significant role in the oxidation. There seems to be no unambiguous evidence supporting their conclusion.

In a previous work we carried out studies on the rate of oxidation of alkenes on V–Sn[8,9] and V–Mo[9] oxides and on their reduction with alkenes, together with ^{18}O tracer studies. These studies, together with structural ones using ESR and X-ray Diffraction, *etc.*, have allowed us to discuss the promoter effect for these systems. In the present work, similar studies have been extended to the oxidation of C_3H_6 on Sn–Mo oxides.

Experimental

Material. Sn–Mo catalysts were prepared as follows. Tin hydroxide precipitates obtained from solutions of tin(II) chloride and ammonia were added to a solution containing a required quantity of ammonium heptamolybdate. The resulting slurry was evaporated with constant stirring, dried, and heated in air at 450 °C. SnO_2 was prepared in a similar manner from a tin hydroxide obtained as described above. MoO_3 was prepared by heating ammonium heptamolybdate in air at 450 °C.

Sn–Mo–M catalysts were prepared by mixing MoO_3 with SnO_2 in a desired ratio and heating the mixture in air at 600 °C for 0.5 h. $^{18}O_2$ (99.1%) was obtained from B.O.C. Limited (U. K.).

Surface areas of catalysts as determined by the BET method were as follows: MoO_3, 1.3—2.0; Sn–Mo(75)(containing Mo in 75 mol%), 18; Sn–Mo(50), 19.5; Sn–Mo(10), 33; SnO_2, 6.8; Sn–Mo(50)–M, 5.1 m^2/g. Prior to measurement, all catalysts were subjected to pretreatment with oxygen at 450 °C.

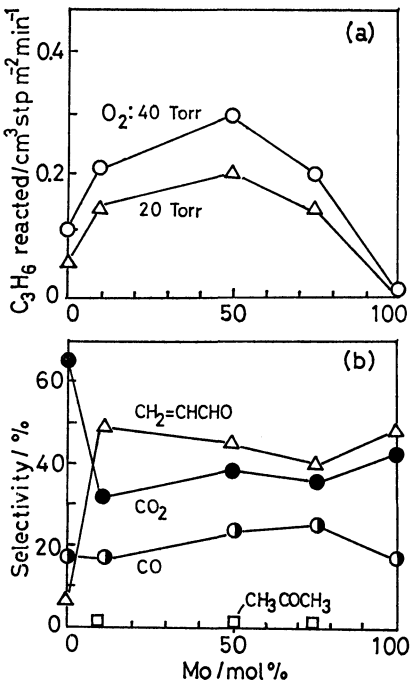

Fig. 1. Rates(a) and product selectivities(b) of C_3H_6 oxidation over Sn–Mo catalysts at 400 °C. $P_{C_3H_6}$= 23 Torr(1 Torr=133.3 N m^{-2}). The product selectivities scarcely changed with oxygen pressure.

Apparatus and Procedure. The catalytic oxidation and the reduction of oxides were carried out in a closed circulation system (320 cm^3). In order to obtain initial rates, conversions were kept below *ca.* 5%. Reaction products such as CH_2=CHCHO, CH_3COCH_3, CO_2, and CO were detected by gas chromatography. The ^{18}O% for a reaction product was determined with a Hitachi RMU-6E mass spectrometer at the following ionization voltages: 80 V for CO and CO_2 and 15 V for CH_2=CHCHO. X-Ray diffraction patterns for catalysts were obtained on a Rigaku-Denki D-3F X-ray diffractometer using Cu $K\alpha$ radiation with a Ni filter. IR spectra of catalysts were recorded on a Hitachi G2 spectrometer, samples being prepared by the KBr pellet technique.

Results and Discussion

C_3H_6 Oxidation over Sn–Mo Oxides and Their Reduction with C_3H_6. Figure 1 shows the rate of oxidation of C_3H_6 and the selectivity for oxidations as a

Table 1. C_3H_6 oxidation over Sn-Mo catalysts

Catalyst (Mo%)	Reaction order		Rate[a] C_3H_6 reacted	Selectivity CH_2=CHCHO
	C_3H_6	O_2	cm^3 stp m^{-2} min^{-1}	%
MoO_3[b]	1.0	0	0.005	50
Sn-Mo(75)	0.1	0.3	0.13	40
Sn-Mo(50)	0	0.4	0.23	40
Sn-Mo(10)	0	0.4	0.15	50
SnO_2	0	0.4	0.09	5

a) $P_{C_3H_6}$=23 Torr, P_{O_2}=20 Torr, and temp 400 °C. b) See Ref. 10.

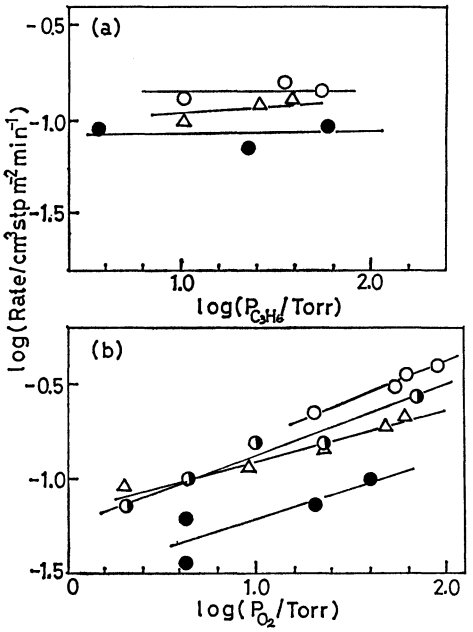

Fig. 2. Dependence of the rate of C_3H_6 oxidation upon C_3H_6 and O_2 pressures over Sn–Mo catalysts at 400 °C. (a) P_{O_2}=20 Torr. (b) $P_{C_3H_6}$=23 Torr. △: Sn-Mo(75), ○: Sn-Mo(50), ◑: Sn-Mo(10), ●: SnO_2.

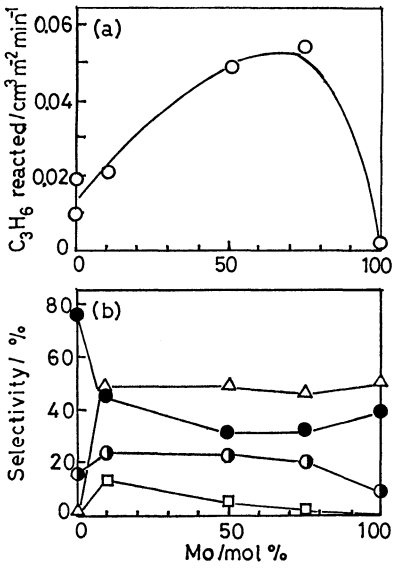

Fig. 3. Reduction of Sn–Mo catalyst with C_3H_6 at 400 °C.
(a) Amount of C_3H_6 reacted. (b) Product selectivities. $P_{C_3H_6}$=23 Torr. Symbols in (b) are the same as those in Fig. 1b.

function of MoO_3 content. The rate of oxidation passes through a maximum, though not pronounced, at Sn–Mo (50). The distribution of products is essentially the same for all the Sn–Mo oxides. The selectivity toward CH_2=CHCHO formation is about 40—50%, the remainder being for CO and CO_2. With SnO_2, the CH_2=CHCHO formation is markedly reduced, while the CO_2 formation is increased. With all the Sn–Mo oxides, formation of CH_3COCH_3 takes place with ratios of CH_3COCH_3 to CH_2=CHCHO less than 0.1 above 400 °C.

Figure 2 shows the dependence of the rate of C_3H_6 oxidation upon O_2 and C_3H_6 pressures, from which reaction orders for the oxidation were determined as shown in Table 1. With MoO_3, the reaction is first order in C_3H_6 and zero order in O_2. It is apparent that the orders for Sn–Mo oxides are similar to those for SnO_2.

Rates of the reduction of Sn–Mo oxides with C_3H_6 were determined in the reaction time range 0.5—3.0 min. Amounts of CO, CO_2, and CH_3COCH_3 formed increase linearly with increasing reaction time, while the CH_2=CHCHO formation takes place practically only in the initial measurement (0.5—1 min), scarcely proceeding any more in later periods. By assuming the initial value to approximate the rate of CH_2=CHCHO formation, yields and distributions were determined as a function of MoO_3 content (Fig. 3). A comparison of the rates of oxidation in the presence and absence of oxygen (Figs. 1 and 3) indicates that there is no marked difference between both the rates of oxidation. Furthermore, essentially the same product distributions are obtained with both the oxidations in the presence and absence of oxygen. This suggests that no adsorbed oxygen plays a significant role in the C_3H_6 oxidation over Sn–Mo oxides. It is therefore concluded that the oxidation proceeds via a redox mechanism, *i.e.*, the repetition of the reduction of oxides with C_3H_6 and their reoxidation with gaseous oxygen. The fact that the oxidation is zero order in C_3H_6 and about half order in O_2, suggests that the reduction of oxides with C_3H_6 is very rapid, the rate-determining step in the oxidation being their reoxidation by gaseous oxygen.

With the Sn–Mo (50) catalyst, initial rates of reduction were determined as a function of C_3H_6 pressure. As shown in Fig. 4, the rate of formation of CH_3COCH_3 increases linearly with increasing pressure of C_3H_6,

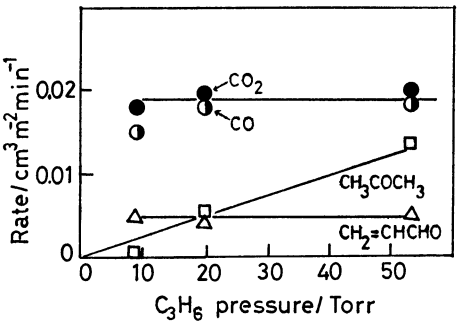

Fig. 4. Variation in the rate of reduction of Sn–Mo(50) with C_3H_6 pressure at 350 °C.

while the rates of formation of CO, CO_2, and CH_2=CHCHO are almost independent of C_3H_6 pressure. These results, together with the fact that the CH_2=CHCHO formation is observed only in the initial measurement, suggest that a very small fraction of the surface is responsible for the reduction, *i.e.*, that the rate for the active part is very large. Such a high rate of reduction is in agreement with the kinetics of the oxidation, *i.e.*, zero order in C_3H_6 and about half order in O_2. Furthermore, it should be noted that essentially the same behavior was observed with the reduction of SnO_2, where reduction products consist of only CO and CO_2.

Structure of Sn–Mo Oxides. According to X-ray diffraction studies, Sn–Mo (10) and Sn–Mo (75) show diffraction lines due only to SnO_2 and MoO_3, respectively. With Sn–Mo (50), lines attributable to SnO_2 as well as MoO_3 appear. No lines indicating any formation of new compounds between SnO_2 and MoO_3 appear, in agreement with results by previous workers.[2,11] The sizes of SnO_2 and MoO_3, as determined from the broadening of diffraction lines,[12] are 15—20 nm and >200 nm, respectively. Intensities of the diffraction lines of MoO_3 in Sn–Mo oxide catalysts were compared with those of mechanical mixtures of MoO_3 and SnO_2. The results indicate that 40—50 mol% of MoO_3 in Sn–Mo (50) and (75) is missing.

In a manner similar to that adopted in a previous work[8] on V–Sn oxides, the intensity of the band due to Mo=O stretching vibration for Sn–Mo oxides was determined as a function of the concentration of Mo ions in KBr pellets. The results are compared with those of similar experiments for MoO_3 (Fig. 5). About 40—50% of MoO_3 in Sn–Mo (50) and (75) exhibits no IR absorption. These results suggest presence of an amorphous material in Sn–Mo (50) and (75) oxides. Although the nature of the amorphous material is unclear, the disappearance of the Mo=O band seems to result from a strong interaction between MoO_3 and SnO_2. No new bands due to the amorphous material are observed to appear. The new bands might be masked by the bands due to SnO_2 or MoO_3. The disappearance of Mo=O band observed with Sn–Mo (10) is attributable to dissolution of Mo ions in SnO_2, as in the case with V–Sn oxides.[8] Okamoto *et al.*[2] have also concluded that the decrease in the crystallinity of MoO_3 in Sn–Mo oxides is attributable to the dissolution of Mo ions in SnO_2 as well as to the

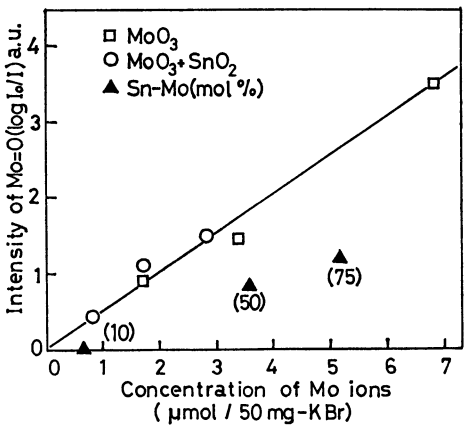

Fig. 5. Estimation of MoO_3 concentration in Sn–Mo oxides.
1 wt% of Sn–Mo oxide in KBr. ○: Mechanical mixture of MoO_3 and SnO_2 at room temperature.

formation of an amorphous material between MoO_3 and SnO_2.

After a heat treatment up to 750 °C the surface area of Sn–Mo (10) decreased from 33 to 25 m^2/g, suggesting a slight increase in the crystal size of SnO_2; no new diffraction lines appeared. With Sn–Mo(50), the intensity of the diffraction lines due to SnO_2 increases by a factor of 1.5, while the MoO_3 crystals grow markedly in the direction perpendicular to the b-axis. Its surface area increases from 19 to 27 m^2/g. In the case of Sn–Mo(75), new diffraction lines due to SnO_2 appear, its surface area increasing from 18 to 29 m^2/g. Such behavior seems explicable in terms of the idea that the amorphous material in Sn–Mo(50) and (75) is decomposed to form SnO_2 and MoO_3, the former crystal being very fine because of its very high melting point. Thus, the presence of amorphous material is confirmed. The lack of any new compounds in Sn–Mo oxides suggests that their promoter effect is attributable to the existence of both Mo ions dissolved in SnO_2 and the amorphous material or of either one.

Catalytic Oxidation of C_3H_6 Using $^{18}O_2$ Tracer. Participation of lattice oxygen in the C_3H_6 oxidation on Sn–Mo oxides was examined by using $^{18}O_2$ as an oxidant instead of ordinary oxygen. No change in the ^{18}O content in oxygen occurred during the reaction, *i.e.*, no formation of $^{18}O^{16}O$ proceeded, which suggests that the exchange of oxygen with the catalyst oxygen is negligible under the present experimental conditions.

As shown in Table 2, with SnO_2 as well as Sn–Mo oxides there is little or no difference between the ^{18}O contents of oxidation products such as CO, CO_2, and CH_2=CHCHO, while with MoO_3 the ^{18}O content of CH_2=CHCHO is larger than those of CO and CO_2. By assuming that the ^{18}O content of H_2O is the average of those of CO, CO_2, and CH_2=CHCHO, for all the oxidation products the ^{18}O content can be determined with each catalyst (Table 2 and Fig. 6).

As previously shown,[9] the feature of the increase in the ^{18}O content of oxidation products with the pro-

TABLE 2. ^{18}O CONTENT IN THE PRODUCTS OF C_3H_6 OXIDATION OVER Sn-Mo OXIDES
$P_{C_3H_6}=23$ Torr (1 Torr$=133.3$ N m^{-2}), $P(^{18}O_2)=8$ Torr, and temp 400 °C

Catalyst	Reaction time / min	Yield/μmol m^{-2} of each product and its ^{18}O content/%[a]			Total yield[b] / μmol-oxygen atoms m^{-2}	Average[c] ^{18}O%	Lattice oxygen[d] participation / μmol m^{-2} (layers)
		CO_2	CO	CH_2=CHCHO			
SnO_2	1	3.0 (40)	0.9 (38)	—	11	40	30 (1—2)
	2.3	7.1 (50)	1.3 (38)	—	24	47	
Sn-Mo(50)	1	4.2 (31)	3.8 (33)	1.8 (35)	24	32	70 (3—4)
	2	9.2 (43)	7.6 (48)	4.5 (48)	51	45	
MoO_3	5.5	2.9 (19)	4.2 (21)	0.8 (33)	19	20	90—150 (4—7)
	15	12.7 (34)	12.7 (39)	3.0 (50)	70	37	

a) Values in parentheses. b) This value was nearly the same as that obtained from the amount of $^{18}O_2$ consumed in the oxidation. c) (Total amount of ^{18}O/total amount of oxygen)$\times$100. d) See Ref. 13.

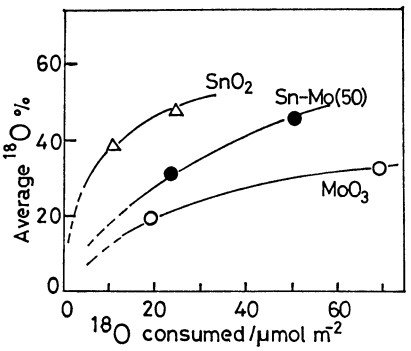

Fig. 6. Average ^{18}O%[a] in the products *vs.* amount oxygen consumed[b] in the oxidation at 400 °C. a),b) See Table 2.

gress of reaction provides information on to what extent lattice oxygen participates in the oxidation. The number of sublayers of the oxide participating in the oxidation was calculated (Table 2), as has been done by Keulks *et al.*[13] The extent of participation of lattice oxygen increases in the order SnO_2<Sn-Mo(50)<MoO_3, while the rate of oxidation on Sn-Mo oxides is about 30 times larger than that on MoO_3. Such features are in contrast to those for Bi-Mo oxides, where the extent of participation of lattice oxygen is in parallel with the rate of oxidation.[13] As regards the nature of such different features, it should be noted that the extent of participation of lattice oxygen for the present system is much smaller than those for Bi-Mo[13] and V-Mo oxides.[9] Furthermore, rate-determining steps for the oxidation differ between Sn-Mo oxides and MoO_3 or Bi-Mo oxides, *etc.*, the reoxidation for the former and the reduction for the latter being the rate-determining step. Accordingly, it appears inappropriate to correlate the catalytic activity solely with the extent of participation of lattice oxygen.

Reduction of ^{18}O Substituted Sn-Mo Oxide and Comparison of Sn-Mo(50) with Sn-Mo(50)-M. Studies of reduction of ^{18}O substituted Sn-Mo oxides with C_3H_6 also are expected to give information on to what extent oxide layers are associated with the reduction of oxides and their reoxidation. Sn-Mo(50), Sn-Mo(50)-M, SnO_2, and MoO_3 were reduced with CO at 400—500 °C, 20—40% of the surface lattice oxygen being removed as CO_2. Then, the reduced oxides were reoxidized with $^{18}O_2$ around 300 °C. The period of reoxidation was 10 h for MoO_3, 2 h for SnO_2, and 2—4 h for Sn-Mo oxides. The amounts of ^{18}O incorporated were nearly the same as those removed by the reduction. As shown in Table 3, the ^{18}O content in products for MoO_3 is much smaller than that for SnO_2, the corresponding values for Sn-Mo oxides being similar to those for SnO_2. These facts indicate that the mobility of lattice oxygen in Sn-Mo oxides as well as in SnO_2 is lower than that in MoO_3.

Table 3 also includes results of similar experiments for Sn-Mo(50)-M, where the ^{18}O content in products is larger than the corresponding values for Sn-Mo(50). Furthermore, the IR band due to the Mo=O vibration for Sn-Mo(50)-M decreased in intensity by about 20% in comparison with 40—50% for Sn-Mo(50). Such behavior would be expected from the difference in preparation procedures between both the Sn-Mo(50) oxides. However, there is little or no difference between the distributions of products of C_3H_6 oxidation for both the oxides, although the rate of oxidation for Sn-Mo(50) is about 1.5 times higher than for Sn-Mo(50)-M. Accordingly, it appears that essentially the same active phase as that for Sn-Mo(50) may be formed for Sn-Mo(50)-M, for example by the heat treatment of a mechanical mixture of SnO_2 and MoO_3 at 600 °C.

The Nature of the Active Phase of Sn-Mo Oxides. As described above, the reduction of Sn-Mo oxides with C_3H_6 proceeds very rapidly as compared to their reoxidation. The results obtained in the present work as well as by Seiyama *et al.*[14] suggest that essentially the same situation is expected for SnO_2. Accordingly, it seems likely that such a high reducibility of Sn-Mo oxides arises from the existence of SnO_2 itself in Sn-Mo oxides. As described above, the active phase of

Table 3. ^{18}O content in the products of the reduction of ^{18}O substituted oxides with C_3H_6. $P_{C_3H_6}=23$ Torr

Catalyst		MoO_3	SnO_2	Sn-Mo(50)-M		Sn-Mo(50)	
Amount of ^{18}O substituted/ μmol m^{-2}		4.9	6.6	6.3	8.0	5.5	5.5
Reduction temp/°C		400	400	350	430	350	430
Reduction time/min		10	5	5	0.5	2	1
Amount of product/ μmol m^{-2}	CO_2	0.10	2.36	0.62	0.62	1.4	2.0
		(<0.5)	(20)	(12)	(7)	(7)	(3)
(^{18}O content/%)	CO	0.062	0.27	0.85	0.80	1.2	1.6
		(<0.5)	(—)	(16)	(11)	(8)	(4)
	CH_2=CHCHO	0.17		0.62	0.84	0.40	0.58
		(<0.5)		(—)	(15)	(13)	(6)
Total amount of lattice oxygen reacted/μmol m^{-2}		0.80	7.6	5.1	5.2	4.0	10.4

Sn–Mo oxides consist of both or either of Mo ions dissolved in SnO_2 and the amorphous material formed from interaction of molybdenum oxide with tin oxide. The results of the reduction of ^{18}O substituted Sn–Mo(50) oxides show that so far as the features of the reduction are concerned, Sn–Mo oxides resemble SnO_2 rather than MoO_3. This suggests that the amorphous material in Sn–Mo oxides can be approximated to some extent by the MoO_3 highly dispersed on SnO_2, where the crystallinity of MoO_3 disappears.

Although the situation is unclear for Sn–Mo(75) which exhibits no diffraction lines due to SnO_2, it is to be noted that there is no marked difference between the rates of oxidation for all the Sn–Mo oxides. In addition, the selectivity for oxidation is essentially the same for all Sn–Mo oxides. This suggests that for Sn–Mo(75) it seems unnecessary to assume the existence of active phases other than the amorphous material (the MoO_3 highly dispersed on SnO_2). Although the active phase of Sn–Mo(10) consists of Mo ions dissolved in SnO_2, there is no marked difference in the surface structures associated with the oxidation between the Mo ions dissolved in SnO_2 and the MoO_3 highly dispersed on SnO_2, since no special features of the C_3H_6 oxidation are observed with Sn–Mo(10).

Such features are out of accord with results of oxidation of alcohols on Sn–Mo oxides described by Okamoto *et al.*[2] who found that the active phase responsible for the oxidation varies according as the composition becomes rich or poor in Mo. According to the work of Niwa *et al.*,[1] however, the rate of oxidation of alcohol on Sn–Mo oxides is independent of the catalyst composition.

Seiyama *et al.*,[14] have shown that there is little or no doubt that on SnO_2 the oxidative dehydrogenation of C_3H_6 to π-allyl species proceeds very easily, whereas the formation of CH_2=CHCHO from the π-allyl hardly takes place. Accordingly, it appears unlikely that the oxygen necessary for the formation of CH_2=CHCHO on Sn–Mo oxides originates from SnO_2; the source of this oxygen seems to be the MoO_3 adjacent to SnO_2. Such a reaction sequence is essentially the same as the model proposed by Haber,[15] who claimed that the formation of π-allyl from C_3H_6 and that of CH_2=CHCHO from π-allyl occur on SnO_2 and MoO_3, respectively. Of course, in the case of Sn–Mo oxides the reactivity of SnO_2 as well as MoO_3 will be enhanced by their mutual contact. In fact the rate of oxidation of C_3H_6 over Sn–Mo oxides is higher than that over SnO_2 as well as MoO_3. Furthermore, the fact that Sn–Mo oxides are 30—40 times more active than MoO_3 but only 4—5 times than SnO_2, is in agreement with what would be expected from the reaction sequence proposed above.

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