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The Nature of Oxygen Species Responsible for Propene Oxidation over V-Mo and V-Sn Oxides

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The rate of oxidation of C_3H_6 has been investigated over V–Mo oxides using $^{18}O_2$(99%) tracer. The extent of participation of lattice oxygen in the oxidation increases with increasing MoO_3 content, showing a maximum at V–Mo (33 mol% of MoO_3) oxide. The rate of oxidation of C_3H_6 varies parallel to the extent of participation of lattice oxygen. A marked dependence of the rate of oxidation upon oxygen pressure observed with V–Mo(33) oxide is attributed to its high reducibility. Similar experiments have been carried out with V–Sn (94 mol% of SnO_2) oxide. The rate of reduction of the oxide with C_3H_6 is about ten times smaller than that of the corresponding catalytic oxidation of C_3H_6, suggesting the participation of adsorbed oxygen in the oxidation. The results of ^{18}O tracer experiments show participation of lattice oxygen in the oxidation. A mechanism which explains such conflicting results has been proposed.

We have recently investigated the rate of oxidation over V–Sn oxides of various compositions.[1] The rate shows two maxima at V–Sn (50 mol% of SnO_2) and V–Sn (94 mol%). It has been concluded that the rate maximum with V–Sn(50) arises from the formation of amorphous material from which lattice oxygen is easily released, participating in the oxidation. However, with V–Sn(94) oxide it is still unclear what oxygen species is responsible for the C_3H_6 oxidation.

There have been a number of work made on the oxidation reaction over V–Mo oxide catalysts.[2–9] It is well known that the rate of oxidation passes through a maximum at 10—30 mol% of MoO_3 and that such maximum activities are often observed under the conditions of high oxygen concentration.[2–6] On the other hand, several workers have observed no maximum activity at these compositions.[7–9] Whether or not the rate maximum is observed appears to be associated with the concentration of oxygen in the reaction mixture. Furthermore, Takita *et al.*[6] have attributed the rate maximum to formation of adsorbed oxygen species which is facilitated by the presence of V^{4+} ions. These appear to remain problems unsolved.

^{18}O Tracer studies appear to be appropriate for the purpose of solving both problems. In the present work, therefore, these studies together with comparison of the rate of oxidation of C_3H_6 in the presence and absence of oxygen have been carried out.

Experimental

Materials. *V-Mo-450 Catalyst*: The solution containing desired quantities of hexaammonium heptamolybdate and ammonium metavanadate was evaporated with constant stirring, and the dried product was calcined in air at 450 °C.

V-Mo-680 Catalyst: A mechanical mixture of V_2O_5 and MoO_3 powders in a desired ratio was melted at 680 °C for 0.5 h, and the melt was ground to powder after cooling. The method of preparation of V–Sn (94) was described previously.[1] $^{18}O_2$ (99.1%) was obtained from B. O. C. Limited (U. K.).

Apparatus and Procedure. The catalytic oxidation and the reduction of the oxides were carried out in a closed circulation system (290 cm³). The reaction products such as acryladehyde, CO_2, and CO were analyzed by gas chromatography.

X-Ray diffraction patterns of the catalysts were obtained on a Rigaku Denki D-3F X-ray diffractometer using Cu *Kα* radiation with a Ni filter. IR spectra of the catalysts were recorded on a Hitachi G2 spectrometer. The samples were prepared by the KBr pellet technique. The ^{18}O% in the reaction products were determined with a Hitachi RMU-6E mass spectrometer using the following ionization voltage; 80 V for CO and CO_2, 16.5 V for H_2O, and 15 V for CH_2=CHCHO. The BET surface area, the IR spectra, and the results of X-ray diffraction analysis are shown in Table 1.

Results and Discussion

C_3H_6 Oxidation over V–Mo Oxides and Their Reduction with C_3H_6. The rates of reduction of V–Mo oxides with C_3H_6 were determined at 320 °C in the range where the plot of the amount reacted *vs.* time is linear (0.5—3 min). The amount of oxygen removed under these conditions corresponded to one or two oxide layers, the distribution of the reaction products being 50% for CO, 35—30% for CO_2, 15—20% for CH_2=CHCHO,

Table 1. Structure of catalysts

	MoO_3 (mol%)	Area/m² g⁻¹	IR spectra (ν/cm⁻¹)	X-Ray diffraction
V-Mo-450	(0)	2.1	1020, 818	V_2O_5
	(33)	3.5	1012, 830, 960	V_2O_5, $Mo_6V_9O_{40}$[a)]
	(50)	4.2	1018, 830, 995, 965	V_2O_5, $Mo_6V_9O_{40}$
V-Mo-680	(0)	1.8	1028, 800	V_2O_5[b)]
	(33)	1.6	1015, 810	V_2O_5[c)], $Mo_6V_9O_{40}$
	(50)	1.0	—, 990—965, 880, 810	$Mo_6V_9O_{40}$
V-Sn(94, SnO_2 mol%)		43	620	SnO_2

a) See Ref. 10. b) Strongly oriented in the direction perpendicular to c axis. c) The distance between the (001) plane was contracted from 4.38 Å to 4.30 Å.

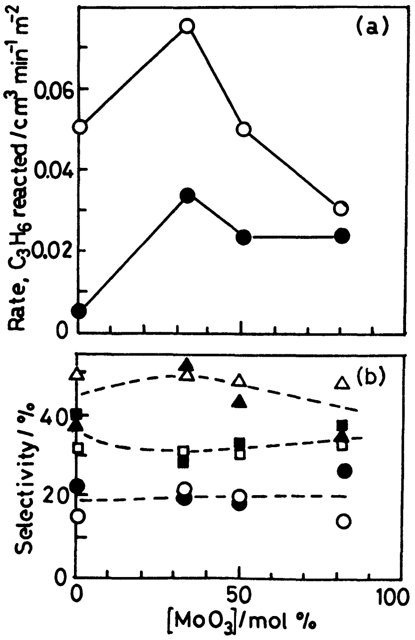

Fig. 1. Reduction of V–Mo oxides with C_3H_6.
(a) Rate. ○: V–Mo-450, ●: V–Mo-680. (b) Selectivity. △, ▲: CO, □, ■: CO_2, ○, ●: CH_2=CHCHO. Closed symbols refer to V–Mo-680. Temp 320 °C, $P_{C_3H_6}$=23 Torr (1 Torr=133.3 N m^{-2}).

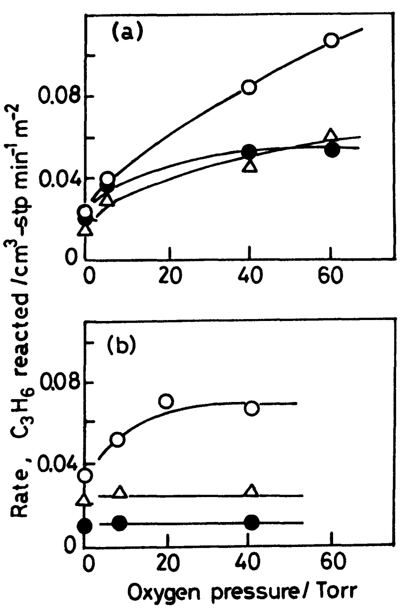

Fig. 2. C_3H_6 oxidation over V–Mo oxides at various oxygen pressures.
Temp 320 °C, ●: V_2O_5, ○: V–Mo (33), △: V–Mo (50). (a) V–Mo-450, $P_{C_3H_6}$=6 Torr. (b) V–Mo-680, $P_{C_3H_6}$=23 Torr.

below 2—3% for CH_3CHO and CH_3COCH_3. Figure 1 shows the rate of reduction thus obtained as a function of MoO_3. With V–Mo-450 as well as V–Mo-680, the rate of reduction passes through a maximum at V–Mo(33) as reported by several workers.[2–6] The product distribution is the same throughout all the catalysts, suggesting that the reduction of vanadium ions is the main reaction. It should be noted that the preparation temperature affects the reducibility of the oxides markedly, *i.e.*, V_2O_5-450 is almost 10 times more reactive than V_2O_5-680, although the V–Mo oxides exhibit no such a marked difference in their reducibility according to their preparation temperature.

TABLE 2. ^{18}O CONTENTS IN THE PRODUCTS OF C_3H_6 OXIDATION OVER V–Mo OXIDES
$P_{C_3H_6}$=23 Torr, $P_{^{18}O_2}$=8 Torr, and temp 320 °C.

Catalyst[a)]	Reaction time min	Yield[b)] of each product and its ^{18}O content (%)[c)] CO_2	CO	H_2O	CH_2=CHCHO	Total yield[e)] µmol-oxygen atoms	Average[f)] ^{18}O/%	Lattice oxygen[g)] participated µmol m^{-2} (layer)
V_2O_5-680	3	1.6	1.6	2.4	0.3	6	8—11	35
		(4.6)	(14)	(–)	(24)			(≈2)
	15	13	6.4	12.5	1.2	33	28	
		(25)	(31)	(–)	(35)			
V–Mo(33)-680	1	5.7	7.5	10.6	0.8	25	5	600
		(4.6)	(5)	(—)	(11)			(≈30)
	3	22	26	37	1.3	90	7	
		(6)	(7)	(3)	(8)			
V–Mo(50)-680	3	11	10	16	0.7	38	8	230
		(6.5)	(6)	(8)	(13)			(≈11)
V_2O_5-450	1	14	15	22	0.9	53	13	180
		(12)	(13)	(11)	(25)			(≈9)
	3	29	32	47	1.5	110	25	
		(25)	(25)	(20)	(31)			
V–Mo(33)-450	1	19	20	29	0.7	70	9	370
		(9)	(8)	(10)	(15)			(≈19)
V–Mo(50)-450	1	14	11	18	1.1	45	8	270
		(8)	(8)	(6)	(14)			(≈13)

a) 2 m^2 of catalyst was used. b) Expressed as µmol of oxygen atoms in each product. c) Values in parentheses. d) Calculated from hydrogen balance. e) This value was nearly the same as that obtained from the amount of $^{18}O_2$ consumed in the oxidation. f) (Total amount of ^{18}O/total amount of oxygen) × 100. g) See Ref. 13.

Figure 2 shows the dependence of the rate of the catalytic oxidation of C_3H_6 over V–Mo oxides upon oxygen pressure. In the oxidation at high pressure of oxygen ($<$40 Torr), the rate of oxidation is higher for V–Mo(33)-450 than for other V–Mo-450 oxides, although the situation is not clear in the low pressure region ($>$6 Torr). Such a behavior reflects the high dependence of the rate of oxidation for V–Mo(33)-450 upon oxygen pressure, *i.e.*, the order of the reaction in oxygen is about 0.4 for V–Mo(33)-450, while 0.3 for other V–Mo oxides. A similar situation is observed with V–Mo-680; The order of the reaction is 0.2 for V–Mo-(33)-680, but zero for other V–Mo-680 oxides. As is shown in Table 2, the product distribution for catalytic oxidation of C_3H_6 is essentially the same as that for the reduction of oxides with C_3H_6, *i.e.*, the oxidation of C_3H_6 in the absence of gaseous oxygen.

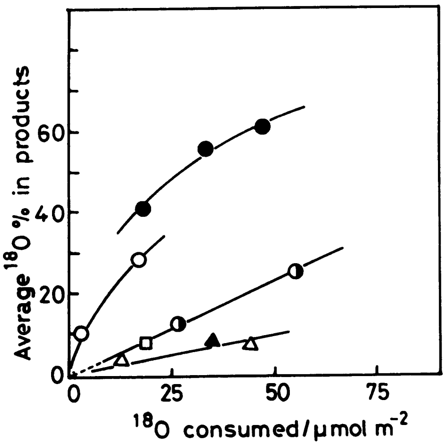

Fig. 3. Average $^{18}O\%^{a)}$ in the products *vs.* amounts of oxygen consumed$^{b)}$ in the oxidation.
○: V_2O_5-680, ◐: V_2O_5-450, △: V–Mo(33)-680, ▲: V–Mo(33)-450, □: V–Mo(50)-680, ●: V–Sn(94). Experimental conditions are the same as in Table 2. a), b) see Table 2.

C_3H_6 Oxidation over V–Mo Oxides Using $^{18}O_2$ Tracer. Table 2 and Fig. 3 show the results of the oxidation experiments using $^{18}O_2$ tracer. The product selectivities towards CO_2, CO, and CH_2=CHCHO are nearly the same as those of the reduction experiments (Fig. 1). No change in the ^{18}O content of the oxygen occurred during the reaction, i.*e.*, no formation of $^{16}O^{18}O$ took place. This suggests that the heterophase exchange[11] of oxygen with the catalyst did not take place. According to the work of Blanchared *et al.*,[12] the exchange of oxygen through CO_2 appears to be negligible under the present experimental conditions.

The ^{18}O content in the products ranges from 5 to 10% at the initial stage of the reaction (Table 2 and Fig. 3), in spite of the use of 99% of $^{18}O_2$ as the reactant. This suggests that lattice oxygen participates in the oxidation. Since the anion vacancies formed by the reduction with C_3H_6 are refilled by gaseous oxygen, the ^{18}O content in the lattice oxygen increases with progress of the oxidation. If only the surface layer of the oxides participates in the oxidation, the increase of the ^{18}O content in the products with progress of the oxidation will be very rapid. On the other hand, if many sublayers participate in the oxidation, the reverse situation will result owing to the dilution of the incorporated ^{18}O with lattice oxygen. Accordingly, the feature of the increase of $^{18}O\%$ in the products provides information to what extent the lattice oxygen participates in the reaction. Furthermore, if only the surface layer of the oxide participates in the oxidation, the surface anion vacancies formed by the reduction are refilled directly by gaseous oxygen without diffusion of the oxide ions in the lattice. On the other hand, when the extent of participation of lattice oxygen is high, most of the surface anion vacancies are refilled by diffusion of oxide ions. This suggests that whether or not the diffusion of the oxide ions is easy appears to be important for determining the extent of participation of lattice oxygen in the oxidation. As has been done by Keulks *et al.*,[13] assuming uniform distribution of the incorporated ^{18}O among the sublayers of the oxides and the number of oxygen atoms in unit area of the surface, the extent of participation of lattice oxygen in the reaction has been calculated (Table 2).

As regards V–Mo-680, the extent of participation of lattice oxygen increases with increasing MoO_3 content, showing a maximum at V–Mo(33), and then it decreases. As shown in Table 1, V–Mo(33) and V–Mo(50) consist of V_2O_5 as well as $Mo_6V_9O_{40}$, and $Mo_6V_9O_{40}$ alone, respectively. It is well known that addition of MoO_3 to V_2O_5 leads to formation of V^{4+},[2] which increases the concentration of anion vacancy in V_2O_5, *i.e.*, makes the diffusion of the oxide ions in the lattice easy. Thus, a marked increase in the participation of lattice oxygen observed with V–Mo(33)-680 is explicable, since the extent of participation of lattice oxygen is associated with the rate of diffusion of the oxide ions as described above. The decrease in the participation of lattice oxygen observed with V–Mo(50) seems to be attributed to formation of $Mo_6V_9O_{40}$ where the diffusion of oxide ions will be more difficult than with V_2O_5.

A similar situation is observed with V–Mo-450. The extent of participation of lattice oxygen is higher for V–Mo(33)-450 than for V–Mo(50)-450. Furthermore, a marked difference between the extent of lattice oxygen participation for V_2O_5-680 and -450 appears to be attributed to a higher concentration of V^{4+} for V_2O_5-450.

It is seen from Table 2 that for both V–Mo-680 and -450 oxides the extent of participation of lattice oxygen runs parallel with the rate of catalytic oxidation of C_3H_6, *i.e.*, for both series of V–Mo oxides the order V_2O_5<V–Mo(50)<V–Mo(33) holds. Such feature is in agreement with that observed with Bi–Mo oxides by Keulks *et al.*[13]

As will be shown later, the participation of lattice oxygen in the oxidation does not always exclude the possibility that adsorbed oxygen participates in the oxidation. Comparison of the rates of C_3H_6 oxidation in the presence and absence of gaseous oxygen is expected to provide information on such possibility (Fig. 2). Since the rates of catalytic oxidation of C_3H_6 over V–Mo oxides vary with the pressure of oxygen, it is difficult to compare both rates of oxidation quantitatively. However, as is seen in Fig. 2, there appears to be no marked difference between both rates of oxidation, suggesting that no adsorbed oxygen plays a significant role in the oxidation over V–Mo oxides.

As has been proposed by a number of workers[15] with Bi–Mo oxides, the reduction of the oxides with C_3H_6 and its oxidation by gaseous oxygen occur in different regions on the surface, A and B, respectively. The surface anion vacancies formed in the region A are refilled by diffusion of the oxide ions in the bulk, which results in formation of the surface anion vacancies in the region B. These vacancies bring about the oxygen uptake. Under such situation, the following equation holds:

$$k_A N_A P_{C_3H_6}\theta_A = k_B N_B P_{O_2}^{1/2}(1-\theta_B),$$

where θ and $1\text{-}\theta$ refer to the surface oxide ions and anion vacancies, respectively.

Similar situation will be expected for V–Mo oxides. Since the rate of oxidation for V–Mo oxides is not independent of oxygen pressure (Fig. 2), the values of θ_A and θ_B are less than unity, in contrast with the case of Bi–Mo oxides where $\theta_A=\theta_B=1$ holds. There appears to be no marked difference between the values of θ_A and θ_B, since the diffusion of the oxide ions will be rapid as compared to the surface reduction. Accordingly, the above equation is transformed as follows:

$$k_1 P_{C_3H_6}\theta = k_2 P_{O_2}^{1/2}(1-\theta),$$

where k_1 is rate constant for reduction step and k_2 for reoxidation step. The following rate equation results:

$$r = k_1 k_2 P_{C_3H_6} P_{O_2}^{1/2}/(k_1 P_{C_3H_6} + k_2 P_{O_2}^{1/2}).$$

This equation has been found to be applicable to the results shown in Fig. 2 with the values of k_1 and k_2 in Table 3. It is seen that with V–Mo-680 as well as V–Mo-450 k_1 is higher for V–Mo(33) than for V–Mo(50) and V_2O_5, while no marked difference in the value of k_2 is observed for all catalysts. Such a high value of k_1 for V–Mo(33) is expected from the order of increasing reducibility of V–Mo oxides, V_2O_5<V–Mo(50)<V–Mo(33) (Fig. 1). Furthermore, it is to be noted that a marked dependence of the rate of oxidation upon oxygen pressure observed with V–Mo(33) is explicable in terms of the concept that the value of k_2/k_1 for V–Mo(33) is smaller than the corresponding value for other catalysts.

Table 3. Values of k_1 and k_2 at 320 °C

	V-Mo-450			V-Mo-680		
MoO_3 (mol%)	(0)	(33)	(50)	(0)	(33)	(50)
k_1[a)]	0.01	0.03	0.01	0.0002	0.003	0.001
k_2[b)]	0.04	0.025	0.03	0.04	0.10	0.10

a) $cm^4\ Torr^{-1}\ min^{-1}\ m^{-2}$. b) $cm^3\ Torr^{-1/2}\ min^{-1}\ m^{-2}$.

The above considerations suggest that the rate maximum for V–Mo(33) oxide results from the weakening of V=O bond[2] and is not attributable to the fact that formation of adsorbed oxygen is facilitated by the presence of V^{4+} ions. In fact, the shifts of the V=O absorption band occur for V–Mo(33)-680 (1028→1015 cm^{-1}) and V–Mo(33)-450(1020→1012 cm^{-1}). The change in the lattice constant of V_2O_5 (d_{001}: 4.38→4.30 Å) has been observed with V–Mo(33)-680 alone. No change in the lattice constant with V–Mo(33)-450 may be attributed to the fact that dissolution of Mo ions into V_2O_5 is confined to the surface region alone.

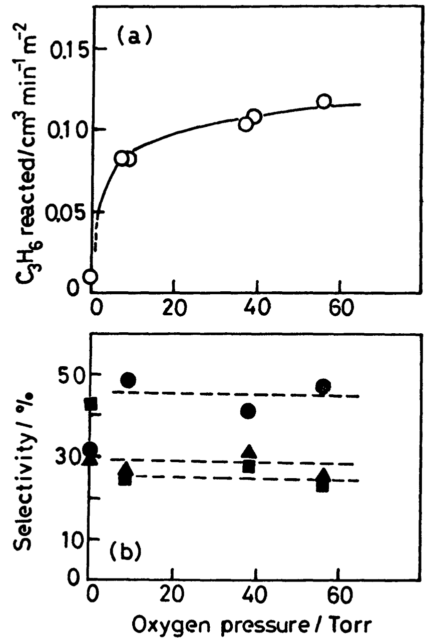

Fig. 4. C_3H_6 oxidation over V–Sn(94) oxide at various oxygen pressures.

(a) Rate. (b) Selectivity. ●: CH_2=CHCHO ▲: CO, ■: CO_2. Temp 320 °C, $P_{C_3H_6}$=23 Torr.

C_3H_6 Oxidation over V–Sn Oxides. Figure 4 shows the rate of C_3H_6 oxidation over V–Sn(94) oxide as a function of oxygen pressure. The rate of oxidation increases slightly with increasing oxygen pressure, the order of the reaction being about 0.1 in oxygen. The rate of reduction of V–Sn(94) oxide with C_3H_6, *i.e.*, the rate of oxidation of C_3H_6 in the absence of oxygen shown in Fig. 4 is 10—12 times smaller than the corresponding catalytic oxidation at 8—60 Torr of oxygen, in contrast with the results for V–Mo oxides where a slight difference is observed between both rates of oxidation. Such a marked difference in the rate of oxidation of C_3H_6 in the presence and absence of oxygen suggests that some active oxygen species may be formed in the presence of gaseous oxygen over V–Sn(94) oxide. Such an active oxygen species may be referred to adsorbed oxygen. As regards adsorbed oxygen, the following case should be mentioned. Some fraction of surface lattice oxygen is more reactive than the remainder; the redox cycle taking place in the presence of oxygen will be limited to such a small fraction. In the absence of oxygen the reaction will occur on the whole surface, including inactive regions. In this case, the enhancement of the rate of oxidation by the presence of oxygen similar to that observed for adsorbed oxygen is expected. Here, such a special type of lattice oxygen is included in the adsorbed oxygen, since it is very difficult to distinguish between both types of oxygen species. The rate of oxidation of C_3H_6 over V–Sn(94) oxide was

TABLE 4. ^{18}O CONTENTS IN THE PRODUCTS OF C_3H_6 OXIDATION OVER V–Sn(94) OXIDE
Experimental conditions are the same as Table 2.

Catalyst[a]	Reaction time / min	Yield[b] of each product and its ^{18}O content (%)[c]				Total yield[e] / μmol-oxygen atoms	Average[f] ^{18}O/%
		CO_2	CO	H_2O[d]	$CH_2=CHCHO$		
V–Sn(94)	0.5	12	6.2	14.2	1.8	35	40
		(38)	(40)	(—)	(40)		
	1.0	27.6	9.8	27.6	4.0	69	57
		(57)	(50)	(—)	(57)		
	2.0	33	20	37	2.6	92	61
		(59)	(62)	(−)	(61)		

a)—f) See Table 2.

found to be independent of C_3H_6 in the range 8—60 Torr. Accordingly, the following rate expression holds $r=kp^{0}_{C_3H_6}P^{0.1}_{O_2}$. Such a low order of the reaction in oxygen as well as in C_3H_6 is different from the feature of the reaction order observed with V_2O_5 and V–Mo oxides.

C_3H_6 Oxidation over V–Sn(94) Oxide Using $^{18}O_2$ Tracer. Table 4 and Fig. 3 show the results of C_3H_6 oxidation using $^{18}O_2$ tracer for V–Sn(94) oxide. The ^{18}O content in the reaction products ranges from 40 to 60%, being much higher than those for V–Mo oxides. There is little or no difference in the ^{18}O content among CO, CO_2, and CH_2=CHCHO. The increase in the ^{18}O content with progress of the reaction is similar to that with V–Mo oxides.

If only adsorbed oxygen participated in the reaction, no incorporation of lattice oxygen in the oxidation would take place, *i.e.*, the ^{18}O content in the products would reach 100%. Such feature has been found by Morooka *et al.*[14] who investigated the oxidation of C_3H_6 over Cu_2O. The observed ^{18}O content in the products for V–Sn(94) oxide (Table 4) suggests that in addition to adsorbed oxygen, lattice oxygen participates in the oxidation. From the data at the reaction time of one minute it is concluded that the rate of incorporation of lattice oxygen (^{16}O) into the oxidation products is about 15 μmol/min m^2, being much larger than the corresponding rate of the oxidation in the absence of oxygen, *i.e.*, the reduction of the oxide with C_3H_6 which is only 2—3 μmol/min m^2 (Fig. 4). Such a marked enhancement of the rate of incorporation of lattice oxygen by the presence of gaseous oxygen suggests that the oxidation by lattice oxygen and by adsorbed oxygen do not proceed independently, *i.e.*, both oxidations are combined with each other in some way. If adsorbed oxygen attacks propene to form a reaction intermediate, which is easily oxidized by lattice oxygen, it would be possible to explain such an enhancement of the rate of incorporation of lattice oxygen by the presence of oxygen. At present, the nature of the reaction intermediate is unclear. A possible adsorbed oxygen appears to be oxygen anion radicals. Kazanskii *et al.*[16] have proposed that the O^- anion radicals can initiate an effective catalytic oxidation of CO over V_2O_5 supported on silica gel. Further study is necessary to clarify the true nature of adsorbed oxygen as well as the reaction intermediate.

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