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Participation of Double Bond Type Lattice Oxygen in Vapor-Phase Catalytic Oxidation of Olefins

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The reactivity of double bond type lattice oxygen $Mo^{6+}{=}O$ in supported molybdena catalyst has been investigated by means of ESR and ir spectroscopy. It has been shown that the double bond oxygen is similar to a free radical oxygen in nature, in contrast to σ-bond oxygen Mo—O—Mo. This character increases as a result of electron transfer from an adsorbed olefin species to a nonbonding atomic orbital of Mo^{6+} with some decrease in the strength of Mo=O bond during vapor-phase oxidation of lower olefins.

The reactivity of the double bond oxygen as a radical increases inversely with the electronegativity of the molybdenum ion as modified with an oxide of a VA group element or of an alkali metal. This was supported by studies of the catalysis of the oxidation of propylene to acrolein, of butadiene to maleic anhydride and the oxidative dehydrogenation of *trans*-2-butene to butadiene. On the other hand, the activity for these reactions of catalyst modified with a high concentration of alkali metal oxide increases with the electronegativity of the alkali metal. This different effect due to the concentration of the alkali metal oxide is also discussed.

INTRODUCTION

In recent years, many correlations have been made between the strength of the metal–oxygen bond of oxidation catalysts and their activity in the oxidation of several type of molecules (*1–5*). It is also known from organic and inorganic chemistry that the reactivity of a bond not only depends on its strength but also on its type. V_2O_5 and MoO_3 have been well known as typical and selective oxidation catalysts for vapor-phase oxidation of various hydrocarbons. Tarama *et al.* (*6–8*) attributed the special activity of V_2O_5 in these oxidations to the inherent nature of double bond type lattice oxygen $V^{5+}{=}O$ which projects out of the catalyst plane. Trifiro *et al.* (*9*) have classified several oxide catalysts according to the nature of the metal–oxygen bond and have drawn attention to the relationship between their activity and the presence of a metal–oxygen bond having double bond character. However, no hypotheses were so far put forward as to how such a metal–oxygen bond or double bond type lattice oxygen might participate in the oxidation reactions. This prompted us to investigate the nature and the reactivity of double bond oxygen $Mo^{6+}{=}O$ formed on supported molybdena catalyst during vapor-phase oxidation of lower olefins. In this paper, the effect of adding an oxide of a VA group element or of an alkali metal has also been studied, especially from the standpoint of the reactivity of the double bond oxygen in the oxidation of propylene, *trans*-2-butene, and butadiene. Furthermore, activity is discussed by considering the electronegativity or acid–base properties of the metal ion on which oxygen species are formed.

EXPERIMENTAL METHODS

Catalytic oxidation of propylene, *trans*-2-butene, or butadiene was carried out using a conventional flow microreactor at

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1 atm pressure. The reactor consisted of a 13-mm-o.d. Pyrex tube, 300 mm long, with a concentric thermowell. The catalyst was diluted with quartz (30–50 mesh) and Raschig rings (2.5 × 2.5 mm) were added above and below the catalyst bed. Heating was accomplished by means of a cylindrical fluidized thermal bath.

Research grade propylene, *trans*-2-butene, and butadiene were used in all experiments. Air was purified by passing through silica-gel and a soda-lime tower to remove water and carbon dioxide. Nitrogen and hydrogen were supplied by commercial cylinders.

Various molybdena catalysts supported on alumina, silica, and titania carriers were prepared using alumina sol, silica sol, or titania gel by the method described in a previous paper (10). Molybdena containing the oxide of a VA group element catalyst supported on α-alumina was prepared by means of impregnation. Preparation of α-alumina was made by evaporating alumina sol on a water bath followed by calcination of the dried mass obtained at 1200°C for 9 hr. α-Alumina was then sieved into 16–32 mesh. An aqueous solution of ammonium paramolybdate was mixed with an aqueous solution of reagent grade 85 wt% H_3PO_4 and the mixture was used to impregnate the α-alumina. The catalyst was then calcined at 540°C for 2 hr in a current of air. MoO_3–P_2O_5 (α-alumina) catalyst was thus obtained. The amount of active component supported was 16 wt% as $MoO_3 + P_2O_5$.

The other catalysts were prepared by the same method, reagent grade Sb_2O_3 (purity 98%), a hot aqueous solution of As_2O_3 (99.8%) or an acidic aqueous solution of extra pure $Bi(NO_3)_3 \cdot 5H_2O$ with a very small amount of reagent grade nitric acid being added as a source of Sb_2O_3, As_2O_3, or Bi_2O_3, respectively. An aqueous solution of extra pure alkali metal hydroxide was used for the preparation of catalysts containing alkali metal oxide. Molybdena (with additive oxide) supported on titania was also prepared similarly, but titania gel was used instead of α-alumina and the catalyst was calcined in an air current at 500°C for 2 hr.

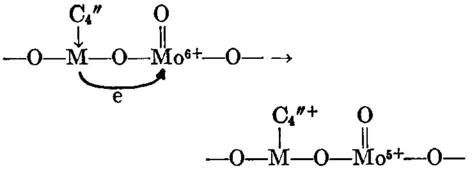
The gaseous effluent from the reactor was analyzed by gas chromatography. PEG 20*M* 20 wt% on Neopak 1A (acrolein, acetaldehyde), $AgNO_3$–ethylene glycol on Neosorb B (propylene), and propylene carbonate 40 wt% on Celite 545 (butenes, butadiene, CO_2) were used as separating columns. Analysis of maleic anhydride was made by titration with an aqueous solution of sodium hydroxide using a pH meter. X-ray diffraction, surface area, ir, and ESR measurements were carried out as described previously (*10*).

RESULTS AND DISCUSSION

Nature of Double Bond Type Lattice Oxygen

A double bond oxygen situated at the surface projects out of the catalyst plane, and therefore it is very likely that this oxygen species is reduced first. Oxidation of hydrocarbons over oxides has long been accepted to proceed through reduction and reoxidation of the catalyst. Oxidation over vanadia or molybdena catalyst is no exception. In the case of molybdena catalyst, double bond oxygen Mo=O is similarly situated at the surface and thus obviously must be reduced first. But further reduction, i.e., reduction of σ-bond oxygen Mo—O—Mo forming Mo^{4+}, seems difficult during vapor-phase oxidation of hydrocarbons because of the presence of larger amount of gaseous oxygen. Hence, reoxidation of the reduced molybdena catalyst proceeds through Mo^{5+} to form the double bond oxygen. However, at the reoxidation step, the following reaction possibly takes place: $\text{-O—Mo}^{5+}\text{—O—Mo}^{5+}\text{—O-} + \frac{1}{2}O_2 \rightarrow \text{-O—Mo}^{6+}\text{=O O=Mo}^{6+}\text{—O-}$ (*11*). Accordingly, it is also likely that the σ-bond oxygen participates in the oxidation reaction via transformation into the double bond oxygen. At any rate, it can be concluded that the double bond oxygen takes part in the oxidation of hydrocarbons more easily than the σ-bond oxygen. Reduction and reoxidation of MoO_3–TiO_2 was already investigated using ir, and the double bond oxygen, which is selective for maleic anhydride formation in vapor-phase oxidation of butadiene, was proved to be reduced more easily than the σ-bond oxygen and to be recovered by reoxidation with air (*10*). Thus, the oxidation of butadiene over MoO_3–TiO_2 seems to proceed through reduction of the double bond oxygen by butadiene and reoxidation of the reduced catalyst by air with formation of the oxygen species. This result provides strong evidence for the participation of double bond oxygen in vapor-phase oxidation of hydrocarbons over molybdena.

It is generally accepted that the oxide catalyst is reduced during the oxidation of hydrocarbons with formation of many free electrons in the bulk. For the purpose of investigating the nature of the double bond oxygen during the oxidation, various supported molybdena catalysts were evacuated at 300°C for 30 min at 10^{-5} mm Hg, and butadiene was adsorbed on these catalysts at room temperature and a pressure of 10 mm Hg. The amount of Mo^{5+} with $g = 1.92$–1.93 (*12*) formed in the catalysts was measured using ESR before and after the adsorption (Table 1). The results clearly demonstrate that Mo^{5+} is formed by electron transfer from the butadiene species adsorbed on the catalyst to Mo^{6+} through the lattice as shown in (a) where M = metal ion:



$$-O-\overset{\overset{C_4''}{\downarrow}}{M}-O-\overset{\overset{O}{\|}}{Mo^{6+}}-O- \rightarrow -O-\overset{\overset{C_4''^{+}}{|}}{M}-O-\overset{\overset{O}{\|}}{Mo^{5+}}-O- \qquad (a)$$

Such an electron transfer has already been suggested by Naccache, Bandiera, and Dufaux in their studies on the adsorption of aromatic hydrocarbons on supported molybdena catalysts (*13*). Krylov and Margolis also proposed such an electron transfer in the formation of O_2^- on the surface of MoO_3–MgO and MoO_3–Al_2O_3 catalysts (*14*). There may be a direct transfer of electrons from butadiene to the adjacent Mo^{6+} ion. But this mechanism seems relatively unlikely as judged from the steric hindrance in the case of butadiene adsorption. Moreover, it was already shown in a previous paper (*15*) that butadiene is adsorbed on Mo^{5+} (not $Mo^{5+}{=}O$) and Ti^{4+} with formation of a slightly positively charged π-complex during the oxidation of butadiene over MoO_3–TiO_2 catalyst. Mo^{6+}, a "hard" metal ion, has a very large electron affinity and so electrons from adsorbed butadiene species are expected to be trapped by this ion. This result gives good evidence for the electron transfer mechanism shown in (a). At higher temperatures, free electrons are also formed by the reduction of the catalyst, and these electrons are probably delocalized in the solid, the $Mo^{5+}{=}O$ ions being thus spread over the whole bulk. However, it is very possible that most $Mo{=}O$ on the surface is $Mo^{5+}{=}O$, because electrons from adsorbed butadiene spread from the surface to the bulk and they are trapped easily by surface $Mo^{6+}{=}O$. Formation of Mo^{5+} is due to the donation of an electron into a nonbonding atomic orbital of Mo^{6+}. The above result clearly suggests that the actual electronic structure of the double bond oxygen during the oxidation of olefins is $Mo^{5+}{=}O$, the double bond oxygen being activated easier than the σ-bond oxygen. Thus, the electron transfer results in a valence shift of Mo^{6+} to Mo^{5+}, and consequently the nature of the oxygen will be allowed to change by some decrease in the electronegativity of the molybdenum ion.

Asmolov and Krylov investigated the structure of supported molybdena by means of ESR and optical diffuse reflectance spectroscopy, and revealed that Mo^{6+} on the surface is present in octahedral coordination (*16*). If the catalyst surface is

TABLE 1
FORMATION OF Mo^{5+} ON BUTADIENE ADSORPTION

Catalyst (0.1 g)	Relative amount of Mo^{5+}	
	Evacuated at 300°C	C_4'' adsorption at 20°C
MoO_3-TiO_2 (1:3)[a]	0.245	0.572
MoO_3-SiO_2 (1:9)	0.080	0.092
MoO_3-Al_2O_3 (2:9)	0.071	0.174

[a] Mole ratio.
C_4'': butadiene.

assumed as xy plane, double bond $Mo^{6+}{=}O$ is formed by the overlapping of one of the octahedron-type atomic orbitals of the molybdenum ion made from sp^3d^2-hybridization with the sp_z-hybridized orbital of the oxygen atom ($\rightarrow$ σ-bond) and by that of the unoccupied d_{zx} of the ion with the $2p_x$ of the atom ($\rightarrow$ π-bond). One electron is accordingly present on the $2p_y$ of the oxygen, two electrons on the σ- and on the π-bond being distributed between the molybdenum and the oxygen. An electron on the $2p_y$ will be also delocalized by overlapping of the $2p_y$ with the d_{yz} of the molybdenum ion. However, these electrons are more localized around the oxygen with formation of Mo^{6+}. So the double bond oxygen looks like a radical oxygen. Electrons from adsorbed olefin species probably transfer into a nonbonding orbital, i.e., d_{xy} or d_{yz} of the hexavalent molybdenum ion.

On the other hand, σ-bond oxygen Mo—O—Mo is made from these two σ-bondings by the overlapping of one octahedron-type atomic orbital with the sp_x-hybridized orbital of the oxygen. This σ-bond oxygen has occupied $2p_y$ and $2p_z$, and thus is not a radical, in contrast to the double bond oxygen. Hence, the double bond oxygen seems to have larger electron affinity than the σ-bond oxygen.

When the electronegativity of the molybdenum ion in $Mo{=}O$ decreases by addition of some modifiers or by electron transfer as just shown, the electrons in the σ and π orbitals are expected to be more localized around the double bond oxygen with some decrease in the bond order or the strength of $Mo{=}O$ bond and also with approach of its oxidation number to -1. Enhancement of the free valence of the oxygen is also to be expected from this decrease in the electronegativity. As the electronegativity is $Mo^{6+} > Mo^{5+}$, the above discussion can be valid in the case of $Mo^{6+}{=}O$ and $Mo^{5+}{=}O$. Therefore, the double bond oxygen in $Mo^{6+}{=}O$, and especially in $Mo^{5+}{=}O$, seems similar to a free radical oxygen in nature, and the strength of the $Mo^{5+}{=}O$ bond is possibly lower than that of $Mo^{6+}{=}O$.

The formation of $Mo^{5+}{=}O$ and the change in the strength of the $Mo{=}O$ bond on butadiene adsorption are supported by ir studies. MoO_3–TiO_2 (3:1) catalyst was finely powdered and evacuated at 250°C for 2 hr at 10^{-5} mm Hg followed by butadiene adsorption at a pressure of 10 cm Hg for 24 hr. After a fixed time of adsorption, the catalyst was taken out at room temperature without evacuation and investigated using ir. The effect of the adsorption temperature on the spectrum of the $Mo{=}O$ bond is shown in Fig. 1. A sharp peak at 992 cm^{-1} due to the stretching vibration of $Mo^{6+}{=}O$ becomes broader with increasing temperature, with formation of a weak hump at 960–970 cm^{-1}. The weak hump also appeared on adsorption at room temperature. Adachi *et al.* observed formation of $Mo^{5+}{=}O$ at 970 cm^{-1} in their studies on the adsorption of formic acid on molybdena using ir (*17*), which provides evidence for the weak hump being attributed to the stretching vibration of $Mo^{5+}{=}O$. Trifiro, Kubelkova, and Pasquon (*18*) also ob-

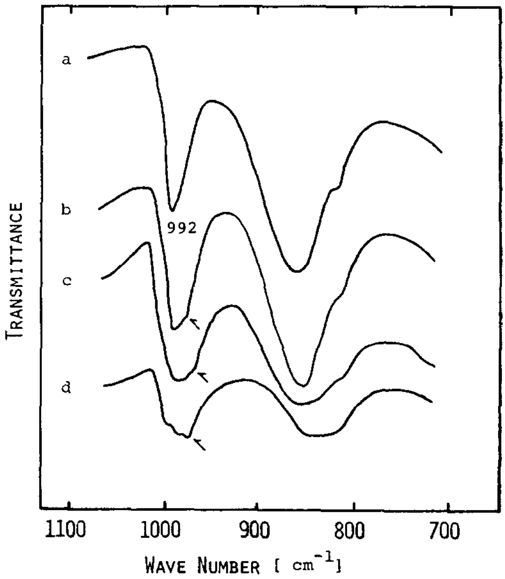


FIG. 1. Effect of butadiene adsorption temperature on the spectrum of $Mo{=}O$. (a) MoO_3–TiO_2 (3:1) evacuated; (b) C_4'' adsorption at 150°C; (c) C_4'' adsorption at 200°C; (d) C_4'' adsorption at 250°C.

served this kind of red shift in their studies on propylene adsorption on molybdena. This result is consistent with those obtained in ESR studies and in quantum-chemical discussions of the Mo=O bond. Thus, it is very likely that Mo^{6+} accepts one electron through the lattice during the oxidation of olefins, forming Mo^{5+}=O, the double bond oxygen behaving like a radical oxygen. The strength of the double bond decreases as a result of the electron transfer.

Effect of VA Group Oxides on the Nature of the Double Bond Oxygen

When molybdena is supported on carriers, it is usually more easy to reduce it. Moreover, as carriers are in general resistant to reduction, it is probable that only Mo^{5+} is formed in supported molybdena, with loss of the double bond oxygen by evacuation at higher temperatures or during the oxidation of hydrocarbons. O_2^- seems to be formed on this Mo^{5+}, as shown by many investigators (*19*). O_2^- was observed on preevacuated MoO_3–TiO_2 catalyst, and its amount showed a very different temperature dependence from that on preevacuated TiO_2 (*10*), being similar to that on MoO_3–Al_2O_3 obtained by Ishii and Matsuura (*19*). This suggests formation of Mo^{5+} without Ti^{3+} over MoO_3–TiO_2 on the evacuation at higher temperatures. The surface Mo^{5+}=O is present in octahedral coordination, and therefore adsorption of gaseous oxygen on this species can be expected to be very difficult, as judged from the viewpoint of steric hindrance. Thus, it can be concluded that only Mo^{5+} species are formed on the surface by the reduction of supported molybdena catalyst, and gaseous oxygen is adsorbed with formation of O_2^-.

Che and Tench (*20*) showed in their ESR studies on O_2^- on supported molybdena that some covalent bonding to the surface cation is involved. As Mo^{5+} has one electron in a t_{2g} orbital (d_{xy}, d_{yz}, d_{zx}) and one unoccupied octahedron-type orbital which projects out of the catalyst plane, the following two mechanisms are possible for oxygen adsorption on Mo^{5+} as judged from the symmetry of the orbitals.

(a) By adsorption of oxygen on Mo^{5+} to give an octahedral coordination, a t_{2g} electron enters the octahedron-type orbital. This orbital overlaps with the sp_z-hybridized orbital of molecular oxygen (nonbonding, occupied by one electron) with a simultaneous overlapping of unoccupied d_{zx} or d_{yz} of the molybdenum ion with π or π^* of molecular oxygen.

(b) Even on the approach of gaseous oxygen to Mo^{5+}, the d electron of Mo^{5+} is kept in a t_{2g} or d_{zx} orbital. The unoccupied octahedron-type orbital overlaps with sp_z of molecular oxygen (nonbonding, occupied by two electrons) with a simultaneous overlapping of d_{zx} or d_{yz} with π^* or π of the oxygen (occupied by one or two electrons). It is not obvious which mechanism plays a role in oxygen adsorption on Mo^{5+}. However, electrons are distributed between the molybdenum and the molecular oxygen according to their electronegativities, possibly more localized around the oxygen rather than the molybdenum ion. One electron is accordingly present in the π^* orbital of the molecular oxygen; thus O_2^- is a radical.

When the electronegativity of the molybdenum ion decreases by the addition of modifiers, the electrons in these orbitals existing between the molybdenum and the oxygen are expected to be more localized around the oxygen with some decrease in the bond order or the strength of the Mo—O_2^- bond, thus making O_2^- unstable. Hence, the amount of O_2^- formed on the modified Mo^{5+} is possibly proportional to the electronegativity of the Mo^{5+}. It is generally accepted that the strength of the metal–oxygen bond and the heat of oxygen adsorption on the metal oxide increase in proportion to the electronegativity of the metal ion (*21*). This supports the result outlined above.

In order to clarify the effect of VA group oxide on the nature of Mo^{5+}, MoO_3–TiO_2 (1:99) catalyst modified with the oxide (50 mg) was evacuated at 520°C for 1 hr at 10^{-5} mm Hg in a quartz tube and then gaseous oxygen (5 mm Hg) was introduced at about −100°C. The change in the amount of O_2^- ($g = 2.019$, 2.009, 2.003) with rise in temperature was determined using ESR, and the maximum amount of O_2 formed on the catalyst is shown in Table 2, where the temperature in parentheses is that giving the maximum amount of O_2^-. The order of the maximum amount of O_2^- [/m²-cat] is $P_2O_5 > As_2O_3 > Sb_2O_3 > Bi_2O_3$, agreeing with the order of the electronegativity of the VA group element. The same result was obtained in the case of X/Mo = 10 at.%. As adsorption of oxygen on X_mO_n-alumina catalyst was scarcely observed, O_2^- species are possibly formed on surface Mo^{5+}. Thus, this result suggests the electronegativity of Mo^{5+} to be Mo^{5+} (Bi) < Mo^{5+} (Sb) < Mo^{5+} (As) < Mo^{5+} (P), addition of these oxides giving electronegativity to Mo^{5+} in proportion to the electronegativity of the VA group element.

It is very natural that the strength of double bond Mo=O and the nature of the double bond oxygen should change by addition of the oxides. According to the result obtained from the discussion of Mo=O bond, the order of free valence on the double bond oxygen is expected to be $Bi_2O_3 > Sb_2O_3 > As_2O_3 > P_2O_5$ as a sequence of modifiers in contrast to that of the strength of the bond. That is to say, the reactivity of the double bond oxygen as a radical increases in inverse proportion to the electronegativity of the molybdenum ion modified with the oxide.

For the purpose of ascertaining the above prediction, ir was used to study the structure of MoO_3-TiO_2 (3:1) modified with oxide and the addition effect of the oxide on the reducibility of the double bond oxygen. A parameter X, the relative decrease of the ir peak due to the stretching vibration of Mo=O to that of Mo—O—Mo, was used to estimate the reducibility of the double bond oxygen (*10*). The modified catalysts were reduced with a stream of hydrogen (50 NTP ml/min) at 450°C for 5 min and X was calculated (Fig. 2). As seen from (b) and (c) in Fig. 2, addition of Bi_2O_3 to the catalyst results in the appearance of new absorption bands at 952, 933, and 900 cm⁻¹, whose intensity increases gradually with Bi_2O_3 content in contrast to that of originally present Mo^{6+}=O. As Bi_2O_3 has no absorption band in this ir range, appearance of these new bands can be attributed to the red shift of the double bond through its interaction with Bi_2O_3. This is further supported by the fact that the new bands easily disappear on reduction and are recovered by reoxidation with air, as shown by (c) and (d) in Fig. 2. A similar result was also

TABLE 2

EFFECT OF OXIDE OF VA GROUP ELEMENT ON THE AMOUNT OF O_2^-

Catalyst	E.N. of VA group element	Maximum amount of O_2^- [a]
P-5[b]	2.1	0.174 (20°C)
As-5	2.0	0.137 (20°C)
Sb-5	1.9	0.02
Bi-5	1.9	0.01

[a] [/m²-cat.].

[b] X/Mo = 5 at.%, X = P, As, Sb, Bi, MoO_3/TiO_2 = 1/99.

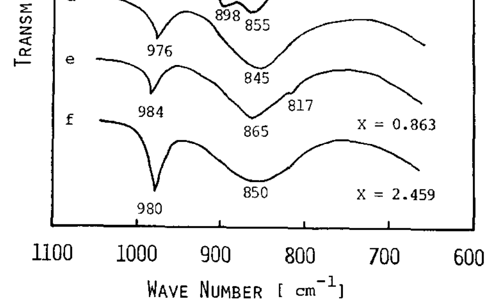


FIG. 2. Infrared spectra of the catalysts. (a) MoO_3-TiO_2 (3:1); (b) Bi/Mo = 15 at.%; (c) Bi/Mo = 30 at.%; (d) Bi/Mo = 30 at.%, reduced; (e) Sb/Mo = 30 at.%, reduced; (f) P/Mo = 30 at.%, reduced.

obtained in the oxidation of propylene over MoO_3–Bi_2O_3 (*22*).

In the case of the other catalysts, a small red shift (3–5 cm^{-1}) of the double bond was observed without any formation of a new absorption band. However, addition of Sb_2O_3 caused easier reducibility of the double bond oxygen ($X < 1$) in contrast to that of P_2O_5 ($X > 1$) as shown in Fig. 2 (e) and (f). As_2O_3 also generated an effect similar to P_2O_5. Thus, the reducibility of the double bond oxygen or strength of the double bond is influenced by the addition of VA oxide, and the order of the reducibility is $Bi_2O_3 > Sb_2O_3 > As_2O_3 > P_2O_5$, a decreasing order of the electronegativity of VA group element as was previously expected.

X-ray analysis of the catalysts revealed that no new compound is formed by addition of Sb_2O_3, As_2O_3, or P_2O_5. In the case of Bi_2O_3, formation of a new compound with $2\Theta = 27.8°$, $29.1°$, ascribable to Bi_2O_3-3 MoO_3 (*23*), was observed and its amount increased with Bi_2O_3 content, which shows that the red shift is due to formation of a new compound.

Oxidation of Propylene to Acrolein and Oxidative Dehydrogenation of Trans-*2-butene to Butadiene*

In oxidative dehydrogenation of butenes over catalysts containing molybdena, lattice oxygen abstracts α-hydrogen from the olefins (*24*) and reactivity of α-hydrogen in various olefins for the oxidative dehydrogenation agrees with that of H^- or $H\cdot$ (*25*). Lattice oxygen is not expected to react with H^-, and accordingly it seems to react with $H\cdot$, possibly through a radical mechanism. This suggests that lattice oxygen acts as a radical oxygen at the transition state of the reaction. Matsuura and Schuit (*26*) studied the adsorption of butenes and butadiene on γ-$Bi_2O_3\cdot MoO_3$ and concluded that lattice oxygen in Bi_2O_3 layers is selective for the oxidative dehydrogenation of butenes. On the contrary, Ohdan *et al.* (*22*) investigated Bi_2O_3–MoO_3 in vapor-phase oxidation of propylene and showed that double bond oxygen Mo=O plays an important role in the oxidation, agreeing with the result obtained by Trifiro *et al.* (*18*), and that addition of Bi_2O_3 only gives rise to some change in the strength of the double bond or the reducibility of the oxygen. It is very likely that the double bond oxygen rather than the σ-bond oxygen participates in these allylic oxidations, behaving as a radical oxygen, and this is supported by the fact that formation of Mo^{5+} was observed during the oxidation of propylene to acrolein over Bi_2O_3–MoO_3 (*27*).

In order to amplify the results obtained in the earlier part of this paper, oxidation of propylene to acrolein and oxidative dehydrogenation of *trans*-2-butene to butadiene were carried out over MoO_3 containing VA oxide, supported on α-alumina, using a differential reactor. The results are shown in Figs. 3 and 4; the ratio of the VA group element to molybdenum in the catalyst is 30 at.%/Mo atom. The yield of *cis*-2-butene and 1-butene was very small (1–7%) relative to that of *trans*-2-butene; hence, most butadiene is possibly formed from *trans*-2-butene.

Figure 3 shows that order of the rate of acrolein formation is $Bi_2O_3 > Sb_2O_3 > As_2O_3 > P_2O_5$. This sequence is in good agreement with a decreasing order of the electronegativity of the VA group element. The rate of butadiene formation is also $Bi_2O_3 > Sb_2O_3 > P_2O_5 > As_2O_3$ (Fig. 4).

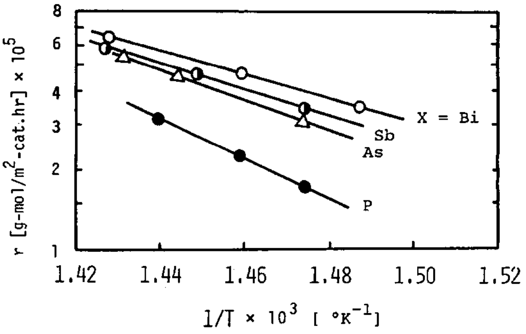


FIG. 3. Rate of acrolein formation in the oxidation of propylene. Feed: propylene 12 vol%, O_2 12 vol%, N_2 76 vol%. Catalyst: X_mO_n–MoO_3 (α-alumina), X/Mo = 30 at.%.

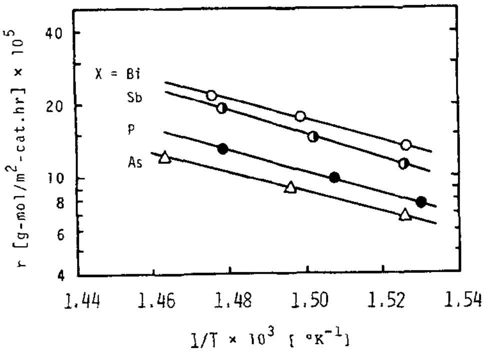


FIG. 4. Rate of butadiene formation in the oxidative dehydrogenation of *trans*-2-butene. Feed: *trans*-2-butene 10 vol%, O_2 10 vol%, N_2 80 vol%. Catalyst: X_mO_n-MoO_3 (α-alumina), X/Mo = 30 at.%.

These results clearly suggest that double bond oxygen Mo=O behaves like a radical oxygen and that it plays the role of abstracting α-hydrogen. Utilization of carbon-13 or -14 already revealed that π-allyl is an intermediate in the oxidation of propylene (*28*). Therefore, it is possible for the double bond oxygen to react with the π-allyl forming acrolein.

In our previous studies on vapor-phase oxidation of butadiene over supported molybdena (*10*, *15*), the double bond oxygen was proved to be selective for maleic anhydride formation and the initial step of the formation was presumed to be addition of the double bond oxygen to the end of adsorbed butadiene species through a radical and ionic mechanism. The addition effect of the oxide of a VA group element on MoO_3–TiO_2 (1:3) in the oxidation of butadiene has now been similarly studied and the rate of maleic anhydride formation from 1.5 vol% butadiene in air determined at 380°C using a differential method (Table 3). The activity sequence is $Bi_2O_3 > Sb_2O_3 > P_2O_5 > As_2O_3$, almost agreeing with the decreasing order of the electronegativity of the VA group element, as was predicted. A similar result was also obtained in the oxidation of butadiene over MoO_3–TiO_2 (1:3) containing a lower concentration of the element than X/Mo = 30 at.%.

TABLE 3

RATE OF MALEIC ANHYDRIDE FORMATION OVER MoO_3-TiO_2 (1:3) CATALYSTS MODIFIED WITH VA GROUP ELEMENTS[a]

VA group element	Surface area [m²/g]	Rate [g mol/m²-cat. hr]
X = Bi	0.2	42.3×10^{-5}
Sb	26	28.8×10^{-5}
As	50	3.6×10^{-5}
P	77	11.1×10^{-5}

[a] X/Mo = 30 at.%, C_4'' 1.5 vol% in air, 380°C.

Effect of Alkali Metal Oxide on the Reactivity of Double Bond Oxygen

When various alkali metal oxides are added to molybdena, an addition effect similar to that of oxides of VA group elements is also expected. As the electronegativity sequence is $Li > Na > K \geq Rb > Cs$, so the reactivity of the double bond oxygen as a radical in molybdena modified with these oxides should be $Cs_2O > Rb_2O \geq K_2O > Na_2O > Li_2O$. In order to examine this prediction, vapor-phase oxidation of butadiene to maleic anhydride, of propylene to acrolein, and oxidative dehydrogenation of *trans*-2-butene to butadiene were investigated over molybdena catalysts modified with a very low con-

TABLE 4

OXIDATION OF PROPYLENE AND *TRANS*-2-BUTENE OVER MoO_3 (α-ALUMINA) CATALYSTS MODIFIED WITH ALKALI METAL ELEMENTS

Alkali metal[a]	Surface area [m²/g]	Rate [g mol/m²-cat. hr]	
		Acrolein[b]	Butadiene[c]
M = Cs	11	13.1×10^{-5}	2.35×10^{-4}
Rb	11	12.9×10^{-5}	2.51×10^{-4}
K	13	10.5×10^{-5}	1.95×10^{-4}
Na	15	10.3×10^{-5}	1.94×10^{-4}
Li	16	8.4×10^{-5}	1.71×10^{-4}

[a] M/Mo = 0.3 at.%.

[b] Feed: propylene 12 vol%, O_2 12 vol%, N_2 76 vol%, 451°C.

[c] Feed: *trans*-2-butene 10 vol%, O_2 10 vol%, N_2 80 vol%, 404°C.

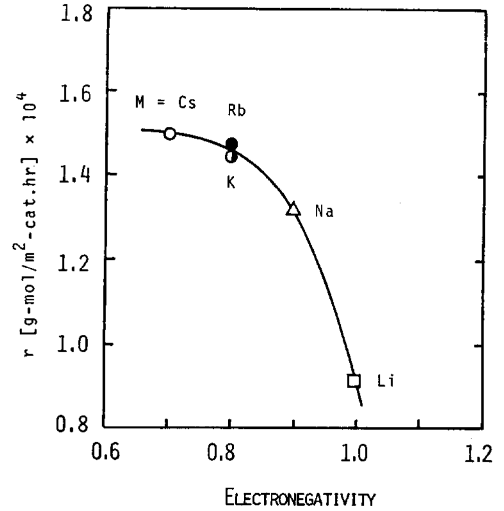


FIG. 5. Rate of maleic anhydride formation in the oxidation of butadiene. Temperature: 365°C, C_4'' 1.5 vol% in air. Catalyst: MoO_3–TiO_2 (1:3), $M/Mo = 1.5$ at.%. Electronegativity, Pauling.

centration of alkali metal oxide using a differential method, and the results are shown in Fig. 5 and Table 4, respectively. The rate of maleic anhydride formation is $Cs_2O > Rb_2O > K_2O > Na_2O > Li_2O$. The rate of acrolein or butadiene formation also follows the same sequence. These results afford strong evidence for the reactivity of the double bond oxygen as a radical in accordance with the case of the oxides of VA group elements.

TABLE 5

OXIDATION OF PROPYLENE OVER MoO_3 (α-ALUMINA) CATALYSTS MODIFIED WITH ALKALI METAL ELEMENTS

Alkali metal[a]	Surface area [m²/g]	Rate [acrolein g mol/m²-cat. hr][b]
M = Cs	17	6.37×10^{-6}
Rb	18	8.93×10^{-6}
K	17	10.1×10^{-6}
Na	18	14.1×10^{-6}
Li	16	28.5×10^{-6}

[a] $M/Mo = 30$ at.%.

[b] Feed: propylene 12 vol%, O_2 12 vol%, N_2 76 vol%, 452°C.

On the other hand, when the concentration of alkali metal oxide increases, a very different result is obtained in the oxidation of propylene and in the oxidative dehydrogenation of *trans*-2-butene. The rate of acrolein or butadiene formation was measured using molybdena-α-alumina modified with 30 at.%/Mo of alkali metal, and the results are shown in Table 5 and Fig. 6. Table 5 indicates the activity of the catalyst for acrolein formation to be $Li_2O > Na_2O > K_2O > Rb_2O > Cs_2O$ in respect of the additives, which agrees with the result obtained in the oxidative dehydrogenation of *trans*-2-butene to butadiene shown in Fig. 6. Thus, the catalytic activity of supported molybdena catalyst modified with a high concentration of alkali metal oxide *increases* with the electronegativity of the metal, in contrast to the case of the very low concentration. Balandin and Sokolova (*29*) showed that tungsten bronze M_xWO_3 ($x < 1$) formed by addition of alkali metal M to WO_3. This compound is possibly formed by electron transfer from the alkali metal to the hexavalent tungsten ion, and therefore its amount seems to increase in inverse proportion to the ioniza-

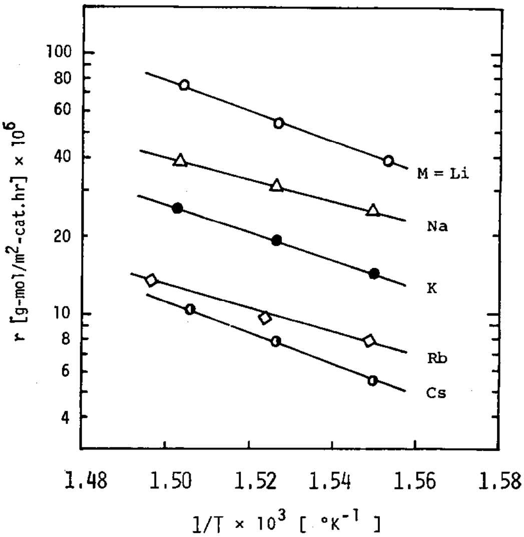


FIG. 6. Rate of butadiene formation over MoO_3 (α-alumina) catalysts modified with alkali metal elements. Feed: *trans*-2-butene 10 vol%, O_2 10 vol%, N_2 80 vol%. Catalyst: M_2O-MoO_3 (α-alumina), $M/Mo = 30$ at.%.

tion potential or the electronegativity of the alkali metal. Formation of this kind of compound by acid–base reaction between M_2O and MoO_3 can presumably be expected in the case of molybdena catalyst, and this compound is possibly inactive for the oxidation reaction. As the amount of the inactive compound is likely to increase inversely with the electronegativity of the alkali metal, the activity of the modified molybdena catalyst in these allylic oxidations becomes $Li_2O > Na_2O > k_2O > Rb_2O > Cs_2O$ in respect of the alkali metal oxide additive, agreeing with the results in Table 5 and Fig. 6. Thus, there are probably two kinds of addition effects on molybdena catalyst in the case of alkali metal oxide: One is the effect of the electronegativity on the reactivity of the double bond oxygen; the other is the formation of inactive compound by acid–base reaction. The two effects will compete. When the concentration of alkali metal is very low, the amount of inactive compound formed should be very small and therefore the former effect presumably plays the more important role in the addition effect. On the other hand, the latter effect may appear strongly over the catalyst with high concentration of the alkali metal. The oxidation of butadiene over MoO_3–TiO_2 (1:3) modified with a high concentration of the oxide was not studied. But, the activity of the catalyst for maleic anhydride formation possibly shows the same sequence as in the reaction of propylene or *trans*-2-butene.

There are some difficulties in the conclusion that the double bond oxygen is similar to a radical oxygen in nature, but many oxidation reactions over molybdena or vanadia catalyst can apparently be explained using this conception. This will be studied further. To sum up, we propose that double bond oxygen Mo=O behaves like a radical oxygen, its radical character increasing especially as a result of electron transfer to a nonbonding atomic orbital of Mo^{6+}, and that its reactivity is strongly affected by the electronegativity or acid–base properties of the molybdenum ion as modified with oxides of VA group elements or alkali metals. The characteristic reactivity of the double bond oxygen in participating in allylic oxidations as a selective oxygen species is attributed to this special nature of the oxygen.

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