

Catalytic Properties of Tricomponent Metal Oxides Having the Scheelite Structure

I. Role of Bulk Diffusion of Lattice Oxide Ions in the Oxidation of Propylene

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Received September 20, 1985; revised May 15, 1985

Kinetic measurements and ¹⁸O₂ tracer studies for evaluating the participation of lattice oxide ions in the oxidation of propylene were carried out for a series of tricomponent metal oxide catalysts having the scheelite structure, Bi_{1-x/3}V_{1-x}Mo_xO₄. Catalytic activity of the scheelite oxide catalysts tested increased with the substitution of V⁵⁺ ion by Mo⁶⁺ ion without changing the selectivity. The kinetic parameters of propylene oxidation to acrolein were found to be unchanged according to Mo content (reaction orders: 1 for propylene and 0 for oxygen, activation energy: 19 ± 0.5 kcal/mol), indicating that the increase of catalytic activity was mainly attributed to the increase of active sites. ¹⁸O₂ tracer studies revealed that lattice oxide ions were exclusively incorporated to form acrolein and CO₂. The diffusion rate of lattice oxide ions in the oxide bulk increased with the increase of X, and then decreased through the maximum at X = 0.45. Good agreement was obtained between the catalytic activity and the mobility of lattice oxide ions. On the basis of the results, the role of the diffusion of lattice oxide ions in the catalytic oxidation is discussed. © 1986 Academic Press, Inc.

INTRODUCTION

Catalytic properties of multicomponent metal oxides for the oxidation of lower olefins have been extensively studied by many investigators (1). Two important developments have been made in understanding the mechanism for the olefin oxidation: (i) α-hydrogen abstraction from the olefin by surface lattice oxide ions is the rate-determining step, followed by the insertion of the lattice oxide ion; (ii) active oxygen on the oxide surface is not supplied from molecular oxygen in the gaseous phase directly but from the internal lattice oxide ion of the catalysts.

Bulk diffusion of lattice oxide ion during catalytic oxidation was first recognized by Keulks (2) and Wragg *et al.* (3) in the oxidation of propylene on catalysts consisting

of group V or VI metal oxides as main constituents. Much attention, therefore, has been paid to this phenomenon but it is still unclear what contribution is made to enhance the catalytic activity by the bulk diffusion of the lattice oxide ion. We have recently investigated the various complex metal oxide catalysts by using ¹⁸O₂ tracer techniques and demonstrated the importance of the diffusion process of lattice oxide ions in supporting excellent catalytic activity of multicomponent metal oxide catalysts and in stabilizing the surface active phase during the redox cycle (4).

In the present study, the catalytic properties of complex metal oxides with scheelite structure, Bi_{1-x/3}V_{1-x}Mo_xO₄, are discussed in the light of the mobility of lattice oxide ions with the aim of understanding the synergistic effect of this catalyst system.

Scheelite-type oxides having cation vacancies are reported by Sleight *et al.* as ac-

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TABLE I

Composition and Surface Area of $\text{Bi}_{1-x}\text{V}_x\text{Mo}_3\text{O}_{12}$

X	Composition	Surface area (m^2/g)
0.00	BiVO_4	1.8
0.09	$\text{Bi}_{0.97}\text{V}_{0.91}\text{Mo}_{0.09}\text{O}_4$	1.4
0.15	$\text{Bi}_{0.95}\text{V}_{0.85}\text{Mo}_{0.15}\text{O}_4$	1.4
0.21	$\text{Bi}_{0.93}\text{V}_{0.79}\text{Mo}_{0.21}\text{O}_4$	2.4
0.27	$\text{Bi}_{0.91}\text{V}_{0.73}\text{Mo}_{0.27}\text{O}_4$	2.4
0.45	$\text{Bi}_{0.85}\text{V}_{0.55}\text{Mo}_{0.45}\text{O}_4$	2.6
1.00	$\text{Bi}_{2/3}\text{MoO}_4$ ($\text{Bi}_2\text{Mo}_3\text{O}_{12}$)	1.8

tive and selective catalysts for the allylic oxidation of olefins (5). Oxides have a simple and uniform structure and the content of the desired constituting elements can be controlled by substitution without changing the fundamental structure. Thus, the catalyst system has been widely examined for the systematic study of catalytic properties.

EXPERIMENTAL

Catalyst preparation. Scheelite catalysts containing bismuth, molybdenum, and vanadium with different compositions were prepared from a mixture of ammonium metavanadate, ammonium heptamolybdate, and bismuth nitrate solution. The powder of ammonium metavanadate was dispersed in a basic ammonium solution (pH 10) of ammonium heptamolybdate. This slurry was mixed with a nitrous solution of bismuth nitrate, followed by the evaporation of water at 80°C . The resulting solid was dried at 110°C and calcined for 4 h at 500°C in an air stream. $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ was prepared according to the method reported elsewhere (1). Every catalyst was confirmed to be monophasic by powder X-ray diffraction patterns which were recorded using an X-ray diffractometer with $\text{CuK}\alpha$ radiation. Semiquantitative information on the surface composition of the catalysts was obtained by XPS spectra recorded using an ESCA spectrometer equipped with an Mg anode ($h\nu = 1251.4 \text{ eV}$) with several as-

sumptions concerning the escape depth and the transmission factor. Composition of scheelite oxide catalysts and the surface area determined by N_2 adsorption at liquid N_2 temperature are listed in Table I.

Apparatus and procedure. Catalytic activity and selectivity for the oxidation of propylene to acrolein and its kinetic parameters were determined by using a conventional flow microreactor under atmospheric pressure (propylene, 6–20%, oxygen 7–25%; nitrogen, balance; reaction temperature, $390\text{--}470^\circ\text{C}$; catalyst weight, 1 g). Propylene oxidation using $^{18}\text{O}_2$ gas was carried out in the circulating glass reactor system under the following standard conditions: initial pressure, $P_{\text{C}_3\text{H}_6} = P_{\text{O}_2} = 70 \text{ Torr}$; reaction temperature, 450°C , catalyst weight, 0.1 g. The reaction gases, $^{18}\text{O}_2$ (British Oxygen, Co., 99.1%) and propylene (Matheson C.P. grade), were used without further purification. The reaction was followed by monitoring the decrease of the pressure and also by quantitative analysis of the gas phase and condensed products which were separated by a cold trap at regular intervals using gas chromatography. The measurement of ^{18}O concentration of molecular oxygen and carbon dioxide in the gas phase and of acrolein in the cold trap was carried out at regular intervals by mass spectrometry. ^{18}O concentration was calculated with the correction for natural isotopes and with the assumption that both normal molecules and isomers containing ^{18}O had the same ionization efficiency.

RESULTS

Kinetics

Figure 1 shows the variations of catalytic activity and selectivity to acrolein in the oxidation of propylene with substitution of V^{5+} ion by Mo^{6+} ion. The activity test of the catalyst in the range of $X = 0.45$ to $X = 1$ could not be carried out because of the failure to make the unit phase oxide.

As already reported in the systemic study of scheelite oxide catalysts by Sleight *et al.*

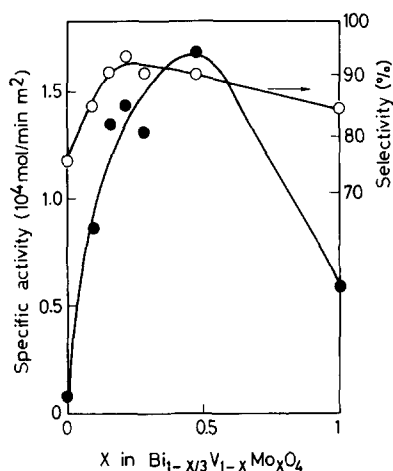


FIG. 1. Catalytic activity and selectivity of scheelite oxide catalysts $\text{Bi}_{1-x/3}\text{V}_{1-x}\text{Mo}_x\text{O}_4$, for the oxidation of propylene to acrolein.

(5), catalytic activity increased drastically with the formation of cation vacancies. However, further substitution to form a high concentration of cation vacancies beyond $X = 0.45$ resulted in the decrease in activity through the maximum which can be seen in Fig. 1. On the other hand, the selectivity of the catalysts tested was slightly affected by the substitution.

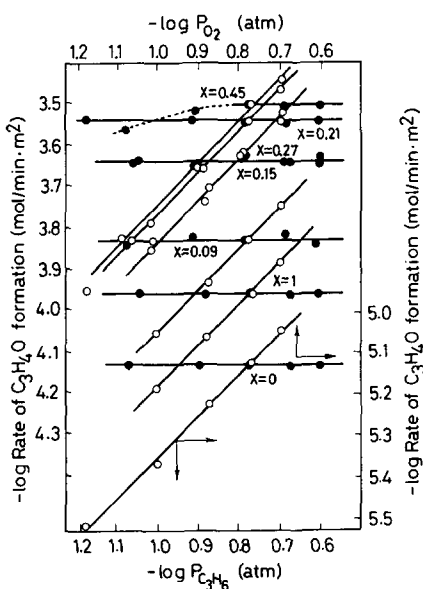


FIG. 2. Dependence of the formation rate of acrolein on propylene and oxygen pressure.

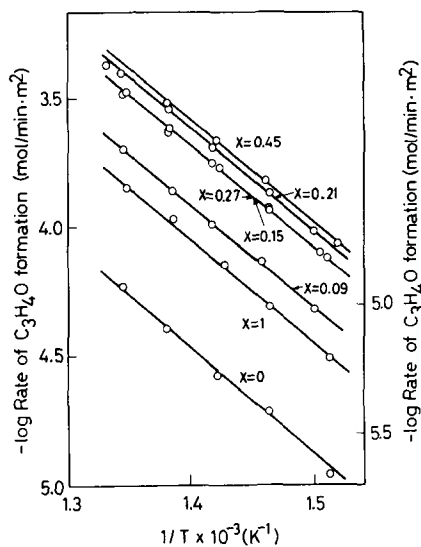


FIG. 3. Arrhenius plots.

Figures 2 and 3 show the kinetic parameters of propylene oxidation, reaction order, and apparent activation energy for every catalyst. Similar to the kinetic results reported previously for the bismuth-molybdenum oxide catalyst system (1), propylene oxidation is first order with respect to propylene and independent of the oxygen pressure under the present reaction conditions, indicating that α -hydrogen abstraction from propylene is the rate-determining step. The apparent activation energy is $19 + 0.5$ kcal/mol for every catalyst. Results in both Figs. 2 and 3 clearly reveal that the reaction kinetics are independent of the Mo content of the catalysts in spite of a drastic change in the specific activity. Thus, the most plausible reason for the increase in the catalytic activity by the introduction of molybdenum to the catalyst is the increase in the number of active sites.

^{18}O Tracer Measurements

Typical results of $^{18}\text{O}_2$ tracer measurements are shown in Fig. 4 for the catalysts ($X = 0, 0.09, 0.45$, and 1). The figures show the changes of ^{18}O concentration in acrolein, carbon dioxide, and gaseous oxygen as a function of reaction time. The ^{18}O con-

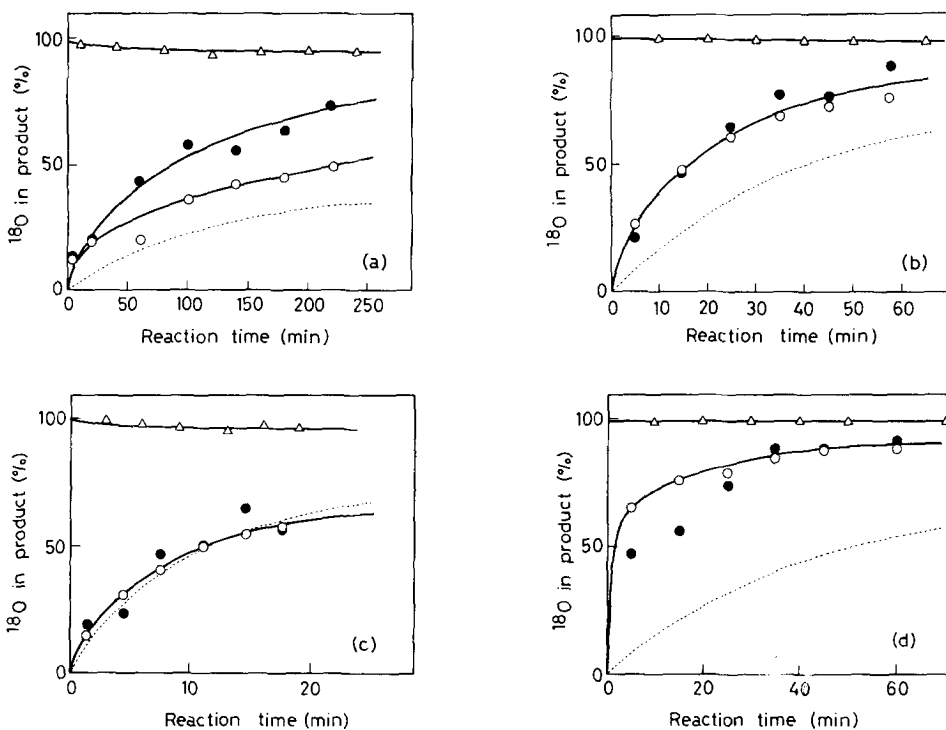


FIG. 4. Incorporation of ^{18}O into the oxidation products of propylene over $\text{Bi}_{1-x}\text{V}_x\text{Mo}_4\text{O}_{13}$. (a) $X = 0$, (b) $X = 0.09$, (c) $X = 0.45$, (d) $X = 1$. \circ , Acrolein; \bullet , carbon dioxide; \triangle , gaseous oxygen. (· · ·) Theoretical curve calculated on the assumption that all lattice oxide ions in the catalyst particle are in rapid equilibrium with the surface active species of oxygen.

centration of carbon dioxide was determined using samples accumulated in the circulating reaction gas. All the data in the figures were converted by the calculation to the differential values corresponding to that of acrolein. Values of gaseous oxygen in the figure are the ^{18}O concentrations of molecular oxygen in the circulating reaction gas during the reaction. The rate of the heterophase exchange reaction between gaseous oxygen and lattice oxide ion in the catalyst was not rapid and the ^{18}O concentration of O_2 was virtually constant during the catalytic oxidation. These characteristics are commonly observed for the complex metal oxides consisting of molybdenum oxide as the main component (4a).

Oxygen atoms in acrolein formed in the initial stages of the reaction were primarily ^{16}O from the lattice oxide ions in the catalyst, but the ^{18}O concentration in acrolein

increased gradually with the reaction time. It is clear that the lattice oxide ion is utilized as the active oxygen for the catalytic oxidation and is exclusively incorporated into acrolein, and that the molecular oxygen, $^{18}\text{O}_2$, is captured by the oxide catalyst to become lattice oxide ions and diluted the ^{16}O concentration in the lattice oxide ions. This is supported by the fact that adsorbed oxygen is hardly detectable on the surface of the scheelite oxide catalyst in the temperature-programmed desorption of oxygen.

^{16}O in the original oxide lattice of the catalyst was also incorporated into carbon dioxide. ^{18}O concentration in CO_2 increased with the reaction time in accord with the change of ^{18}O concentration in acrolein over every scheelite catalyst except for BiVO_4 . This result reveals that the lattice oxide ion is also active for the formation of

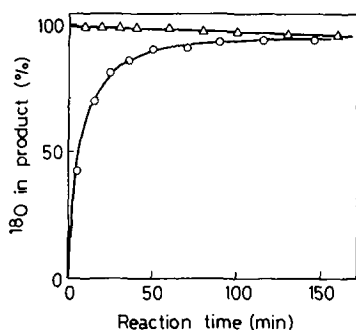


Fig. 5. Incorporation of ^{18}O into the oxidation products of propylene over $\text{Bi}_{0.93}\text{V}_{0.79}\text{Mo}_{0.21}\text{O}_4$ catalyst. Catalyst weight, 0.03 g. \circ , Acrolein; \triangle , gaseous oxygen.

carbon dioxide. It is, however, difficult to find any difference in the incorporation of ^{16}O into acrolein and carbon dioxide. In BiVO_4 , ^{18}O concentration in CO_2 was higher than that in acrolein as can be seen in Fig. 4a. This may be due to the significant exchange reaction between oxygen atoms formed in carbon dioxide and lattice oxide ions during the longer reaction time because of low catalytic activity.

Dotted lines in the figures are hypothetical; they show the changes in the ^{18}O concentration of the products under the complete mixing of all lattice oxide ions in the catalysts with the surface active species of oxygen. The difference between the actual and hypothetical lines seems to depend on the composition of the catalyst. In the case of $\text{Bi}_{0.85}\text{V}_{0.55}\text{Mo}_{0.45}\text{O}_4$ catalyst (Fig. 4c), the observed change of the ^{18}O concentration in the oxidized products lies fairly close to the dotted line, indicating the rapid diffusion of lattice oxide ions during the catalysis and the complete mixing of all lattice oxide ions in the catalyst particles. Precise estimation of the mobility of lattice oxide ions is carried out in next section.

Figure 5 shows the result of an $^{18}\text{O}_2$ tracer experiment on the catalyst ($X = 0.21$). The reaction was continued until the ^{18}O concentration in the oxidized products coincided with that in gaseous oxygen. The summation of the number of ^{16}O atoms in the oxidized products, acrolein, CO_2 , and H_2O , and also in gaseous oxygen corre-

sponds to 93% of the total lattice oxide ions in the catalyst when the ^{18}O concentration of the oxidized products reached that of the gaseous oxygen. This indicates that most of the lattice oxide ions can take part in the oxidation of propylene and that all ^{16}O in the virgin oxide catalyst can eventually be replaced with incoming ^{18}O from the gas phase during the oxidation.

Estimation of the Mobility of Lattice Oxide Ions

The mobility of lattice oxide ions in the scheelite oxide during the catalytic oxidation of propylene was estimated from the $^{18}\text{O}_2$ tracer measurements. As mentioned above, molecular oxygen participates in the reaction after being captured in the oxide catalyst as lattice oxide ions and scrambling with inner lattice oxide ions. The increase of ^{18}O concentration in oxidized products with reaction time, therefore, depends on the extent of the scrambling of the lattice oxide ions during the reaction, which may reflect the mobility of lattice oxide ions. However, it seems quite difficult to determine the quantitative correlation between the bulk diffusion rate of lattice oxide ions and the results obtained in the $^{18}\text{O}_2$ tracer experiment. When we continue the reaction under $^{18}\text{O}_2$ gas for a prolonged time, all ^{16}O oxide ions in the catalyst may finally be incorporated into the reaction products as shown in Fig. 5. However, this does not mean all bulk oxide ions are in rapid equilibrium with surface active oxygen. Thus, a more reliable correlation may be obtained from the initial rate of increase in ^{18}O concentration in the products versus the consumption of molecular oxygen for the oxidation.

For the purpose of assuming the mobility of lattice oxide ions, we measured the amount of lattice oxide ions with which the incoming $^{18}\text{O}_2$ equilibrates instantly. This quantity can be regarded as the dilution volume or complete mixing volume of lattice oxide ion, ^{16}O , in the catalyst for the ^{18}O flux through the catalyst. By assuming the

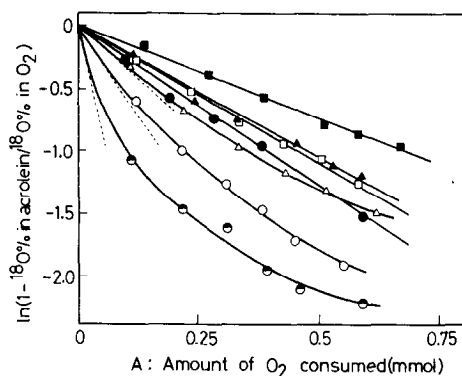


FIG. 6. Plots of the left-hand side of Eq. (2) versus the amount of consumed oxygen. \circ , BiVO_4 ; \triangle , $\text{Bi}_{0.97}\text{V}_{0.91}\text{Mo}_{0.09}\text{O}_4$; \bullet , $\text{Bi}_{0.95}\text{V}_{0.85}\text{Mo}_{0.15}\text{O}_4$; \blacktriangle , $\text{Bi}_{0.93}\text{V}_{0.79}\text{Mo}_{0.21}\text{O}_4$; \square , $\text{Bi}_{0.91}\text{V}_{0.73}\text{Mo}_{0.27}\text{O}_4$; \blacksquare , $\text{Bi}_{0.85}\text{V}_{0.55}\text{Mo}_{0.45}\text{O}_4$; \ominus , $\text{Bi}_2\text{Mo}_3\text{O}_{12}$.

^{18}O concentration of the lattice oxide ions in a dilution volume of catalyst is equal to that in oxidized products in the propylene oxidation at a given time, the complete mixing volume can be calculated from the results of $^{18}\text{O}_2$ tracer experiments by using the complete mixing volume equation

$$\frac{^{18}\text{O}\% \text{ in product}}{^{18}\text{O}\% \text{ in gaseous oxygen}} = 1 - \exp(-A/V) \quad (1)$$

which has been already used by Keulks *et al.* in the investigation of the reactivity of lattice oxide ions of selective oxidation catalysts (6). In this equation, A is the total amount of molecular oxygen consumed in the oxidation of propylene, which equals the total amount (in mol) of ^{18}O flux through the catalyst, and V is the complete mixing volume (in mol). Equation (1) is rewritten as

$$\ln \left[1 - \frac{^{18}\text{O}\% \text{ in product}}{^{18}\text{O}\% \text{ in gaseous oxygen}} \right] = -A/V. \quad (2)$$

Since the heterophase exchange reaction between the gaseous oxygen and the lattice oxide ions was hardly observed during the propylene oxidation, the calculation was carried out by assuming that the ^{18}O concentration in gaseous oxygen was constant.

The plots of the quantity of the left-hand side of Eq. (2) versus A are shown in Fig. 6 for every catalyst tested. The straight lines were obtained for all the catalysts except $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and BiVO_4 . The fact that no straight lines were obtained for $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and BiVO_4 indicates the low mobility of the lattice oxide ion. Incorporated ^{18}O distributes in the vicinity of the surface layer and its concentration decreases exponentially with the increase in distance from the surface. This distribution may be homogenized by the slow migration of the lattice oxide ion. Therefore, the V values for these catalysts are calculated from the initial slope of the obtained curve.

The fraction of the complete mixing volume to the total amount of lattice oxide ions in the catalyst was calculated by using the calculation method mentioned above. The obtained values are plotted in Fig. 7 as a

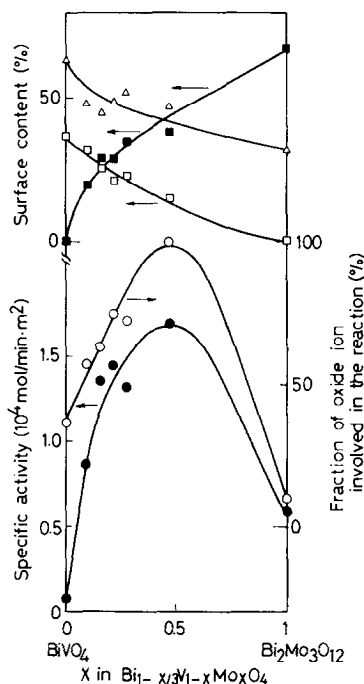


FIG. 7. Comparison of the specific activity of $\text{Bi}_{1-x/3}\text{V}_{1-x}\text{Mo}_x\text{O}_4$ catalysts with the fraction of lattice oxide ions involved in the oxidation of propylene to the total lattice oxide ions in the catalyst particles and with surface content ($M/\text{Bi} + V + \text{Mo}$) of the constituent determined by XPS. \triangle , Bi; \square , V; \blacksquare , Mo.

TABLE 2

Comparison of the Catalytic Activity and Selectivity to Acrolein with the Fraction of Lattice Oxide Ion Involved in the Oxidation of Propylene over $\text{Bi}_{1-x/3}\text{V}_{1-x}\text{Mo}_x\text{O}_4$ Catalysts

X	Specific activity (10^{-4} mol/min · m ²)	Selectivity to acrolein (%)	Fraction of lattice oxide ion involved in the reaction (%)
0.00	0.08	75.6	37.0
0.09	0.87	85.1	57.4
0.15	1.35	91.1	63.0
0.21	1.43	93.7	75.1
0.27	1.31	90.8	72.2
0.45	1.69	90.8	100
1.00	0.59	84.4	10.2

function of the bismuth content of the catalyst with the catalytic activity and surface compositions of every constituent given for comparison. Mobility of lattice oxide ions in the bulk oxide increased with increasing X and then decreased through the maximum at $X = 0.45$ in spite of no substantial change in the catalyst structure. In the catalyst which showed the maximum mobility ($X = 0.45$), the surface active oxygen species are mixed completely with the whole bulk oxide ions under the catalytic reaction conditions.

DISCUSSION

Role of the Lattice Oxide Ion in the Catalytic Reaction

The importance of the diffusion of the lattice oxide ion in the catalytic properties of oxide catalysts for olefin oxidation was first demonstrated by Keulks *et al.* [1a]. They observed a good dependence of the catalytic activity of molybdenum-based oxide catalysts on the mobility of the lattice oxide ion. However, it has remained obscure why rapid migration of the lattice oxide ion increases the catalytic activity. In addition, each catalyst tested by Keulks *et al.* has a different crystal structure and, therefore, the comparison might include not only the

effect of diffusion of the oxide ion but also many other factors.

In the scheelite oxide system studied in this work, the fundamental structure of the catalyst is almost the same for the entire range of catalyst compositions, and the kinetic parameters and the activation energy are independent of the composition (Figs. 2 and 3). On the other hand, we obtained a good correlation between the specific activity and the mobility of lattice oxide ions, as revealed from the comparison between the specific activity of each catalyst tested and the fraction of the lattice oxide ions involved in the reaction (Fig. 7). The results, therefore, permit us to relate the catalytic activity to the mobility of the lattice oxide ion exclusively.

Sleight *et al.* demonstrated that the increase in the catalytic activity by the combination of metal elements is attributed to the high proton acceptability of the cation vacancy introduced by the combination (5). The explanation by Sleight *et al.* is based on the increase in the active sites with the formation of cation vacancies. The kinetic results obtained in the present study are consistent with their interpretation. However, the specific activity of $\text{Bi}_2\text{Mo}_3\text{O}_{12}$, which contains the highest concentration of cation vacancy among the $\text{Bi}_{1-x/3}\text{V}_{1-x}\text{Mo}_x\text{O}_4$ catalyst system, is not high compared to the other catalysts. Cation vacancy, therefore, is not always enough to contribute the active sites necessary for the selective oxidation of propylene.

The kinetic results clearly show that the increase of the catalytic activity by the introduction of molybdenum to the catalyst is attributable to the increase in the number of active sites. However, no clear correlation was observed between the surface concentration of each constituent determined by XPS analysis and the specific activity (Fig. 7). Consequently, the facts observed in the present study suggest that we should consider some direct effect of the bulk diffusion of the lattice oxide ion on the specific activity.

Since the surface of the multicomponent oxide catalyst is not uniform and homogeneous, there must be several kinds of active sites on the catalyst surface; some of them can activate the molecular oxygen and others promote the hydrogen abstraction and oxygen addition more effectively (11, 12). If active sites are isolated from each other and migration of active oxygen is slow, each site has to do everything necessary to form acrolein. This situation may be inconvenient to increase the surface concentration of active sites, because most of the surface sites do not work well under the reaction conditions in such a case. When active species of oxygen can move rapidly through the bulk, equalization of the chemical potential of active oxygen may be attained at any time on all sites of the catalyst surface. Collaboration between different kinds of sites proceeds quite easily; one site activates molecular oxygen exclusively and another site mainly consumes it to oxidize propylene. Since the catalyst surface repeats the reduction and reoxidation cycle continuously during the reaction, this equalization of the chemical potential may prevent over-reduction of the catalyst and thus increases the stability of active composite oxide in the catalyst system as well as enhancing catalytic activity. The experimental evidence for the increase in catalyst life by the rapid diffusion of the lattice oxide ion during catalysis will be described in the accompanying paper.

Diffusion Mechanism of Lattice Oxide Ions in the Scheelite Catalyst

It is well known that higher concentrations of mobile ions and preferable structures for lowering the energy barrier of ion migration are required for solid ion conductors. In the case of an oxygen ion conductor, oxygen anion vacancies are usually involved in the lattices of metal oxides. Higher concentrations of oxygen anion vacancies are introduced by valence control in the stabilized zirconium oxide or perovskite which is widely used as the ox-

xygen ion conductor (7, 8). Rare earth oxides also show mobility of lattice oxide ions because these oxides usually contain oxygen anion vacancies due to their nonstoichiometric composition (9). Mobility of lattice oxide ions is observed in the oxides of the group V and VI metals, such as V_2O_5 and MoO_3 , which are used as active components in the partial oxidation catalysts of olefins. Lattice oxide anions diffuse in these substoichiometric oxides when the oxygen anion vacancies are produced in the lattice under reductive conditions at high temperature.

The scheelite oxide catalysts showed the high mobility of lattice oxide ions during the catalysis. This oxide, however, does not fill the structural demand as an oxygen ion conductor. Although the mobility of the lattice oxide ions in the scheelite oxide catalysts increased by the introduction of cation vacancy as shown in Fig. 7, the enhancement of the mobility is not ascribed directly to the formation of cation vacancy. Then, we discussed the following diffusion mechanism of lattice oxide ions in the scheelite oxides.

The structure of scheelite oxide, $Bi_{1-x/3}V_{1-x}Mo_xO_4$, may be viewed as an assemblage of tetrahedrally coordinated V (or Mo)O₄ units and Bi cations. All Vi-O (or Mo-O) bonds are equal in length and eight oxygen ions are coordinated to the Bi cation from eight different tetrahedra. When cation vacancies are introduced randomly in the lattice by replacing a V cation with a Mo cation, some of the oxygen anions are freed from Bi cations and the tetrahedra may be distorted to some extent. This results in the formation of V=O (or Mo=O) bonds and also in the formation of an oxygen ion shared structure. The formation of doubly bonded oxygen by introducing a cation vacancy has already been confirmed by Raman and IR studies (10). In this structural state, the replacement of shared oxygen anions between tetrahedra seems to be possible when oxygen anions are formed on the oxide surface during the

catalytic oxidation. This process may result in the rapid diffusion of lattice oxide ions. Consequently, it may be concluded that the tetrahedra sharing which arose from the formation of cation vacancies accelerates the migration of lattice oxide ions in the scheelite oxides. If all tetrahedra are undistorted and unshared with each other, the structure seems to be unfavorable for the lattice oxide ion movement. This may be responsible for the low mobility of oxide ion in BiVO_4 . The low mobility of the lattice oxide ion in $\text{Bi}_2\text{Mo}_3\text{O}_{12}$, in spite of having the highest concentration of cation vacancies in the scheelite oxide system, may be due to the formation of ordered cation vacancies which are not true defects.

ACKNOWLEDGMENTS

We thank Nitto Chemical Industry Co., LTD for XPS measurement. Financial support for this work was generously provided in part by a grant from the Asahi Glass Foundation for Industrial Technology.

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