

Study of Ternary-Component Bismuth Molybdate Catalysts by $^{18}\text{O}_2$ Tracer in the Oxidation of Propylene to Acrolein

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Received December 12, 1980; revised March 24, 1981

Participation of lattice oxide ions of ternary-component bismuth molybdate catalysts M-Bi-Mo-O (M = Ni, Co, Mg, Mn, Ca, Sr, Ba, and Pb) was investigated using the $^{18}\text{O}_2$ tracer in the selective oxidation of propylene to acrolein. The participation of the lattice oxide ions in the oxidation is prominent on every catalyst but the extent of the participation varies significantly depending on the structure of the catalyst. Only lattice oxide ions in the bismuth molybdate phase are incorporated into the oxidized products on the catalysts (M = Ni, Co, Mg, and Mn) where M have smaller ionic radius than Bi^{3+} ; catalyst particles are composed of a shell of bismuth molybdates and a core of MMoO_4 . On the other hand, whole oxide ions in the active particles are involved in the oxidation on catalysts having a scheelite-type structure (M = Ca, Sr, Ba, and Pb) where M has a comparable ionic radius to Bi^{3+} .

INTRODUCTION

The multicomponent molybdate catalysts containing bismuth have been known as the most active and selective catalysts for the allylic oxidation of olefins and are used widely in the industrial oxidation of propylene (1). The structure and catalytic behavior of these catalysts were investigated by Wolfs and Batist (2) who suggested that the active species is bismuth molybdate which forms an outer shell on a core of $\text{M}^{\text{II}}\text{MoO}_4$. This model was supported by Matsuura and Wolfs (3) using photoelectron spectroscopy.

On the other hand, Keulks (4) and Wragg *et al.* (5) using $^{18}\text{O}_2$ tracer demonstrated that lattice oxide ions take part in the oxidation of propylene to form acrolein on the bismuth molybdate catalyst. Further investigations have revealed that the lattice oxide ions are incorporated into the oxidation products in several complex oxides (6-9).

The present study was undertaken to clarify the role of each component in the multicomponent bismuth molybdate catalysts using the $^{18}\text{O}_2$ tracer technique developed by Keulks and Wragg *et al.* Before studying commercial catalysts, we examined various ternary bismuth molybdate catalysts having one metal component other than bismuth and molybdenum. This paper identifies what kind of lattice oxide ion is involved in the oxidation of propylene and the effects of the lattice oxide ions on the catalytic behavior of these ternary-component bismuth molybdate systems.

EXPERIMENTAL

Catalyst Preparation

Three Co-Bi-Mo-O catalysts having different compositions were prepared from cobalt and bismuth nitrate solutions and molybdic acid by the method reported by Wolfs and Batist (2). Each mixed slurry was solidified by evaporation, dried at 110°C , calcined in air at 320°C for 1.5 h, and calcined again for 2 h at 520°C .

$\text{M}_{11/12}^{\text{II}}\text{Bi}_{1/12}\text{MoO}_{4+x}$ (M = Ni, Mg, Mn,

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Ca, Sr, Ba, and Pb) and two other Pb–Bi–Mo–O catalysts having different compositions were prepared from bismuth and the corresponding metal nitrate solutions and molybdic acid in a manner similar to that for Co–Bi–Mo–O catalysts.

Apparatus and Procedure

All oxidation runs were carried out using the conventional closed circulating system having a volume of 400 ml. The reactor consisted of 4-mm-o.d. U-shape tubing and was heated in a tabular furnace. The reaction temperature was measured by a thermocouple inserted into the catalyst bed and controlled within $\pm 1^\circ\text{C}$. Tracer experiments were run at 70 Torr of $^{18}\text{O}_2$ pressure and at the same pressure of propylene. The $^{18}\text{O}_2$ gas (British Oxygen Company, 99.1%) and propylene (Matheson C.P. grade) were used without further treatment. The condensable products, acrolein and water, were separated from the reaction gas by cold traps coupled to the reactor exit through an eight-way cock. Two traps were

used alternatively at regular time intervals and each sample condensed in the traps was transferred through an eight-way cock to the vessel for gas chromatography and mass spectrometry. Gaseous oxygen and carbon dioxide were sampled from the circulating reaction gas at the same intervals. The reaction was followed by monitoring the decrease of pressure and also by quantitative analysis using gas chromatography (Porapak T, 3 m, 120°C ; molecular sieve 5A, 0.5 m, 25°C). The ^{18}O concentrations of gaseous oxygen, acrolein, and carbon dioxide were determined by mass spectra obtained at an ionization voltage of 80. A correction was made for natural isotopes, assuming the same ionization efficiency for both the normal molecules and the isomers containing ^{18}O . The ^{18}O concentration of water was also measured but it was difficult to determine exact values because of isotope exchange in the mass spectrometer.

Catalyst Characterization

Summarized in Table 1 are (a) the BET

TABLE 1
Characterization of the Catalysts and the Reaction Conditions for the Tracer Experiment^a

Catalyst		Reaction				
Composition	Phase by X ray	Surface area (m ² /g)	Time (min)	Conversion (%)	Activity (10 ⁻⁵ mol/min · m ²)	Selectivity (%)
Co _{7/8} Bi _{1/8} MoO _{4+x}	CoMoO ₄ , Bi ₂ (MoO ₄) ₃	2.6	210	62	2.2	97
Co _{11/12} Bi _{1/12} MoO _{4+x}	CoMoO ₄ , Bi ₂ (MoO ₄) ₃	3.8	120	39	1.2	97
Co _{17/18} Bi _{1/18} MoO _{4+x}	CoMoO ₄ , Bi ₂ (MoO ₄) ₃	4.7	80	33	1.5	97
Mn _{11/12} Bi _{1/12} MoO _{4+x}	MnMoO ₄ , Bi ₂ (MoO ₄) ₃	1.5	270	41	1.6	96
Mg _{11/12} Bi _{1/12} MoO _{4+x}	MgMoO ₄ , Bi ₂ (MoO ₄) ₃	3.1	60	38	3.3	93
Ni _{11/12} Bi _{1/12} MoO _{4+x}	NiMoO ₄ , Bi ₂ MoO ₆	7.3	20	35	3.8	71
Ca _{11/12} Bi _{1/12} MoO _{4+x}	CaMoO ₄ , MoO ₃	2.7	50	42	4.8	97
Sr _{11/12} Bi _{1/12} MoO _{4+x}	SrMoO ₄	2.5	30	34	9.1	81
Ba _{11/12} Bi _{1/12} MoO _{4+x}	BaMoO ₄	1.6	70	35	5.6	87
Pb _{7/8} Bi _{1/8} MoO _{4+x}	PbMoO ₄	0.5	100	40	11.8	72 ^b
Pb _{11/12} Bi _{1/12} MoO _{4+x}	PbMoO ₄	0.3	180	32	10.0	74 ^b
Pb _{29/30} Bi _{1/30} MoO _{4+x}	PbMoO ₄	0.4	180	39	8.3	70 ^b

^a All runs were carried out at 450°C using 0.1 g of catalysts. Initial pressure: $P_{\text{C}_3\text{H}_6} = P_{\text{O}_2} = 70$ Torr.

^b C₆ olefins were formed as by-products (10–23%).

TABLE 2

Comparison of the Catalytic Activity and Selectivity between Various $\text{M}_{11/12}\text{Bi}_{1/12}\text{MoO}_{4+x}$ and MMoO_4 Catalysts in the Oxidation of Propylene to Acrolein^a

M	$\text{M}_{11/12}\text{Bi}_{1/12}\text{MoO}_{4+x}$		MMoO_4	
	Activity (10^{-5} mol/min · m ²)	Selectivity to acrolein (%)	Activity (10^{-5} mol/min · m ²)	Selectivity to acrolein (%)
Co	1.2	97	0.73	46
Mn	1.8	96	1.2	60
Mg	3.3	93	0.47	64
Ni	3.8	71	3.2	53
Ca	4.8	97	0.024	0
Sr	9.1	81	0.039	0
Ba	5.6	87	0.026	0
Pb	10.0	74 ^b	0.056	26

^a All runs were carried out at 450°C using 0.1 g of catalysts under the initial pressures, $P_{\text{C}_3\text{H}_6} = P_{\text{O}_2} = 70$ Torr.

^b C_6 olefins were formed as by-products (23%).

surface area, (b) the catalyst phase determined by X-ray analysis, (c) the reaction condition for the tracer experiment, and (d) the catalytic activity and selectivity to acrolein of each catalyst.

A comparison of the catalytic behavior differences between simple metal molybdate $\text{M}^{\text{II}}\text{MoO}_4$ and the corresponding ternary-component systems $\text{M}_{11/12}^{\text{II}}\text{Bi}_{1/12}\text{MoO}_{4+x}$ was carried out under the same reaction conditions. Oxidation of propylene was not selective on NiMoO_4 , MgMoO_4 , CoMoO_4 , and MnMoO_4 even under the condition of low single-pass conversion using the microreactor. CaMoO_4 , SrMoO_4 , BaMoO_4 , and PbMoO_4 were almost inactive under the conditions adopted in this experiment. As already reported in patents, selectivity to acrolein on Ni, Mg, Co, and MnMoO_4 is increased significantly by the addition of the bismuth component. In the cases of Ca, Sr, Ba, and PbMoO_4 , both activity and selectivity were improved remarkably as reported by Aykan *et al.* (10) and Sleight (11). The results are summarized in Table 2. The stability of each catalyst was confirmed by X-ray analysis before and after the reaction. No change in

the diffraction pattern was observed after use. It was also confirmed that the catalytic activity did not change after repeated runs.

RESULTS AND DISCUSSION

The diffusion rate of the oxide ion in the bulk of the catalyst was first determined by Keulks and Krenzke for several catalytic systems containing molybdenum and was discussed in connection with the selectivity to acrolein (8, 9). However, the diffusion rate is only measurable for a catalyst having a uniform phase, whereas a number of practical catalysts are composed of multiphase structures. For these catalyst systems having a multiphase structure, it is important to identify the catalyst phase whose lattice oxide ion is exclusively involved in the oxidation. To clarify this problem, the ^{18}O content of the oxidized products was evaluated against two other factors: (i) the total amount of oxygen consumed in the oxidation, and (ii) the total amount of ^{16}O incorporated into the oxygenated products from the catalyst. Both these quantities are expressed as the unit of oxide ion layer of catalysts as follows,

assuming 1×10^{19} oxygen atoms/m² surface area:

$$\Omega_{\text{total-O}} = \frac{\text{Total oxygen atoms consumed in the oxidation}}{(\text{Total surface area of the catalyst used}) \times 10^{19}}$$

$$\Omega_{^{16}\text{O}} = \frac{\text{Total } ^{16}\text{O incorporated into the oxygenated products and gaseous oxygen}}{(\text{Total surface area of the catalyst used}) \times 10^{19}}$$

The ¹⁸O concentration of carbon dioxide was determined using samples accumulated in the circulating reaction gas. Each datum was converted by a calculation to the differential value corresponding to that of acrolein. The ¹⁸O concentration of gaseous oxygen was also measured and plotted in the figures. Slow heterophase exchange reaction between gaseous oxygen and the catalyst was observed in every run. Another oxygen exchange reaction between carbon dioxide and the catalyst was also observed under the conditions used in the oxidation. Fortunately, both exchange reactions were slow and did not exert any serious effect on the evaluation of the participation of the lattice oxide ion in the oxidation of propylene.

The ¹⁸O concentrations in the oxidation products and in the gaseous oxygen are plotted against the reaction time as well as $\Omega_{\text{total-O}}$ and $\Omega_{^{16}\text{O}}$ in Figs. 1, 2, 4, and 5. It is seen that participation of the lattice oxide

ions is quite profound for every catalyst tested. This is in contrast to the results observed on Sb-Fe-O systems where only a few layers of the lattice oxide ion participated in the selective oxidation of propylene to acrolein (12). Although the lattice oxide ions are extensively involved in oxidation in the M-Bi-Mo-O systems, the degree of participation varies significantly, depending on the structure of the catalyst system. These results are discussed below for the two prominent structures of catalyst particles previously reported for M-Bi-Mo-O systems (2, 3, 10, 11).

Catalysts Composed of the Core and Shell Structure, M^{II}-Bi-Mo-O System (M^{II} = Ni, Co, Mg, and Mn)

Ternary-component bismuth molybdate catalysts containing Ni, Co, Mg, or Mn showed very similar catalytic behavior in the oxidation of propylene using ¹⁸O₂ tracer. Typical changes of the ¹⁸O concentration of the oxidation products are shown in Figs. 1 and 2 for Mg-Bi-Mo-O and Co-Bi-Mo-O catalysts. As can be seen in the figures, ¹⁶O from the bulk of the catalyst is clearly incorporated into both acrolein and carbon dioxide in the initial stage of the reaction. The observed ¹⁸O concentration of the carbon dioxide seems to be somewhat lower than that of acrolein on Mg-Bi-Mo-O and Co-Bi-Mo-O catalysts. Since the formation of carbon dioxide is quite low, less than 10% of converted propylene on these two systems, it is not clear whether the difference is essential or is induced by some experimental error. Nevertheless, it seems reasonable to infer that

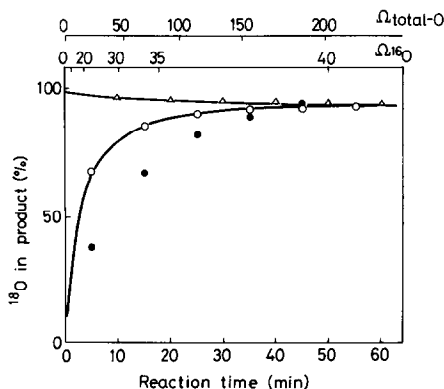


FIG. 1. Incorporation of ¹⁸O into the oxidation products of propylene over Mg_{1.1/12}Bi_{1.1/12}MoO_{4+x} catalyst. ○, acrolein; ●, carbon dioxide; △, gaseous oxygen.

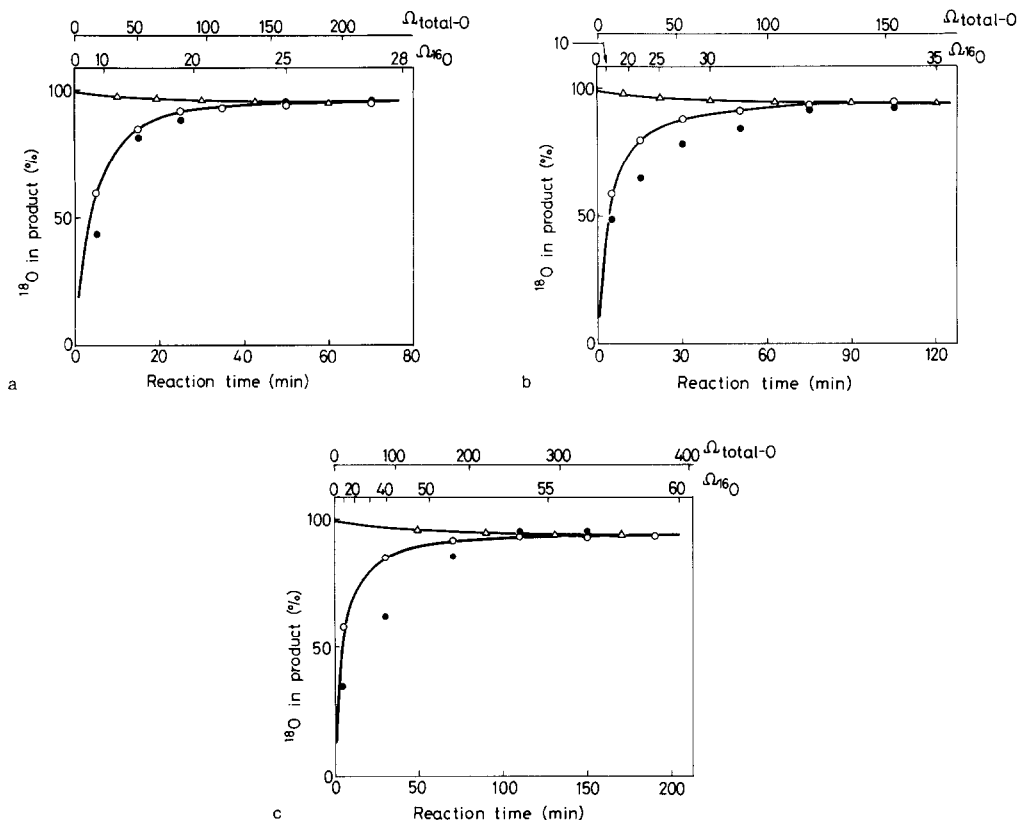


FIG. 2. Incorporation of ^{18}O into the oxidation products of propylene over Co-Bi-Mo-O systems. \circ , acrolein; \bullet , carbon dioxide; \triangle , gaseous oxygen. (a) $\text{Co}_{17/18}\text{Bi}_{1/18}\text{MoO}_{4+x}$. (b) $\text{Co}_{11/12}\text{Bi}_{1/12}\text{MoO}_{4+x}$. (c) $\text{Co}_{7/8}\text{Bi}_{1/8}\text{MoO}_{4+x}$.

participation of lattice oxide ions affects the ^{18}O concentration of the acrolein. Although participation of lattice oxide ions in the oxidation is clear for these catalysts, incorporation of the original lattice oxide ions terminates after a while and the ^{18}O content of the oxidized products reaches the same value as that of gaseous oxygen. At this stage, the accumulated amounts of ^{16}O in the reaction products, $\Omega_{^{16}\text{O}}$, are equivalent to less than about 50 oxygen ion layers of the catalyst. Thus, it is clear that only a part of the lattice oxide ions can participate in the oxidation of propylene. In the case of Co-Bi-Mo-O systems, participation of the lattice oxide ion was examined at three different concentrations of bismuth. The amount of the available lattice oxide ion increases with increase of bismuth content

but still remains only a fraction of the whole of the lattice oxide ions in the catalysts. In Fig. 3, the accumulated amounts of ^{16}O in the reaction products are plotted against the total consumed gaseous oxygen in the reaction. Since the available light oxide ions are limited, the plots show saturation and the amount of oxide ion that can participate in the oxidation is estimated quantitatively for each catalyst. The values are shown in the second column of Table 3.

The results obtained in the tracer experiment are well understood on the model of multicomponent bismuth molybdate catalysts presented by Wolfs and Batist (2). $\text{M}^{\text{II}}\text{MoO}_4$ where M^{II} have smaller ionic radius [Ni^{2+} (0.69), Mg^{2+} (0.66), Co^{2+} (0.72), and Mn^{2+} (0.80)] assume $\alpha\text{-CoMoO}_4$ structure (NiMoO_4) or $\alpha\text{-MnMoO}_4$ structure

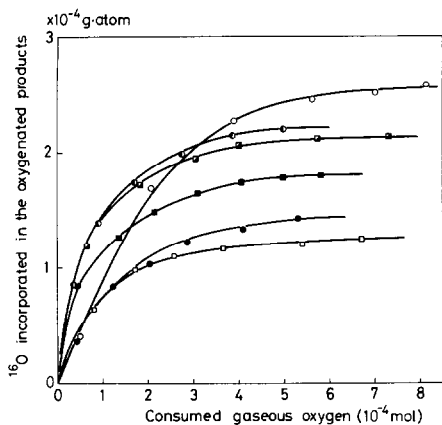


FIG. 3. Change of the amount of ^{16}O incorporated into the oxidation products against the total consumed oxygen in the oxidation of propylene. \circ , $\text{Co}_{7/8}\text{Bi}_{1/8}\text{MoO}_{4+x}$; \circ , $\text{Co}_{11/12}\text{Bi}_{1/12}\text{MoO}_{4+x}$; \bullet , $\text{Co}_{17/18}\text{Bi}_{1/18}\text{MoO}_{4+x}$; \blacksquare , $\text{Mn}_{11/12}\text{Bi}_{1/12}\text{MoO}_{4+x}$; \blacksquare , $\text{Mg}_{11/12}\text{Bi}_{1/12}\text{MoO}_{4+x}$; \square , $\text{Ni}_{11/12}\text{Bi}_{1/12}\text{MoO}_{4+x}$.

(MgMoO_4 , CoMoO_4 , and MnMoO_4). On the other hand, the ionic radius of Bi^{3+} is 0.96 Å and because of this, $\text{Bi}_2(\text{MoO}_4)_3$ and Bi_2MoO_6 have scheelite and keochlinitic structures, respectively. No solid solutions or composite oxides are known between these $\text{M}^{\text{II}}\text{MoO}_4$ and bismuth molybdates. It has been reported that particles of the multicomponent bismuth molybdate catalysts are composed of a core of $\text{M}^{\text{II}}\text{MoO}_4$ and a shell of bismuth molybdates. This model

was confirmed by Matsuura and Wolfs by photoelectron spectroscopy (3) and the catalytic activity was essentially connected with the shell structure (13). In this experiment, each phase corresponding to the model was identified by X-ray analysis. The amount of lattice oxide ion which can participate in the oxidation is compared to the quantities of oxide ion in the bismuth molybdate phase and in the whole oxides. As can be seen in Table 3, the values in the second column are much smaller than those in the last column but almost comparable to the corresponding values in the third column. Thus, it is concluded that only in the bismuth molybdate phase are the lattice oxide ions mobile to the active surface and participate in the oxidation to form acrolein and carbon dioxide. This conclusion seems to be reasonable by reference to the diffusion rates of lattice oxide ion in CoMoO_4 determined by Keulks and Krenzke (8).

Recently, Matsuura and co-workers studied the surface composition of bismuth molybdate catalysts by changing the ratio of bismuth to molybdenum over a wide range (14). They reported that the ratio of bismuth to molybdenum at the surface of the active catalysts is nearly unity irrespective of the bulk composition and that the β

TABLE 3

Comparison between the Total Amount of ^{16}O Incorporated into the Oxidized Products and $^{16}\text{O}_{\text{lattice}}^{2-}$ in the Bi-Mo-O Phase of the M-Bi-Mo-O (M = Co, Mn, Mg, and Ni) Catalysts

Catalyst	^{16}O incorporated into the oxidized products ((g-atom) $\times 10^4$)	$^{16}\text{O}_{\text{lattice}}^{2-}$ in catalyst ^a	
		Bi-Mo-O phase ^b ((g-atom) $\times 10^4$)	Whole catalyst ((g-atom) $\times 10^4$)
$\text{Co}_{7/8}\text{Bi}_{1/8}\text{MoO}_{4+x}$	2.56	3.16	16.8
$\text{Co}_{11/12}\text{Bi}_{1/12}\text{MoO}_{4+x}$	2.20	2.12	17.3
$\text{Co}_{17/18}\text{Bi}_{1/18}\text{MoO}_{4+x}$	1.42	1.46	17.6
$\text{Mn}_{11/12}\text{Bi}_{1/12}\text{MoO}_{4+x}$	1.80	2.20	17.6
$\text{Mg}_{11/12}\text{Bi}_{1/12}\text{MoO}_{4+x}$	2.14	2.50	20.0
$\text{Ni}_{11/12}\text{Bi}_{1/12}\text{MoO}_{4+x}$	1.24	1.08	17.3

^a Amount of $^{16}\text{O}_{\text{lattice}}^{2-}$ in 0.1 g of each catalyst.

^b $\text{Bi}_2(\text{MoO}_4)_3$ phase (M = Co, Mn, and Mg) and Bi_2MoO_6 phase (M = Ni) in the M-Bi-Mo-O catalysts.

phase of bismuth molybdate is the most active for the allylic oxidation of olefins. Since no lattice oxide ions in Ni-, Mg-, Co-, or MnMoO_4 participate in the oxidation, the main role of these metal molybdates seems to be to support and stabilize the active bismuth molybdate phase. It is known that iron or some trivalent metal molybdates are contained as necessary components of practical multicomponent bismuth molybdate catalysts. We found that the participation of lattice oxide ions spreads over all the metal molybdates in the core of catalyst particles when the trivalent metal ion is added to the ternary M-Bi-Mo-O systems examined in this experiment. The effect of trivalent ions on these systems will be discussed in a subsequent paper (15).

*Catalysts Having Scheelite Structure,
 $\text{M}^{\text{II}}\text{-Bi-Mo-O}$ System ($\text{M}^{\text{II}} = \text{Ca}, \text{Sr},$
 $\text{Ba}, \text{and Pb}$)*

$\text{M}^{\text{II}}\text{MoO}_4$ where M^{II} have larger ionic radius [Ca^{2+} (0.99), Sr^{2+} (1.13), Ba^{2+} (1.35), and Pb^{2+} (1.20 Å)] assume a scheelite structure. Ternary-component bismuth molybdate catalysts containing these metal ions also show excellent activity and selectivity for the allylic oxidation of olefins (10, 11). Typical results of the tracer experiment for these catalysts are shown in Figs. 4 and 5. In these cases, the ^{18}O content of acrolein coincided with that of carbon dioxide in all runs using the $^{18}\text{O}_2$ tracer. In contrast to the results obtained on the former M-Bi-Mo-O systems ($\text{M} = \text{Ni}, \text{Mg}, \text{Co}, \text{and Mn}$), the original lattice oxide ions in the catalysts were never consumed within the reaction time of the experiment. Incorporation of ^{16}O still continues after the amount of ^{16}O accumulated in the reaction products, $\Omega_{^{16}\text{O}}$, reaches a value corresponding to several hundred layers of oxide ion as shown in the figures. Broken lines in the figures show hypothetical changes of ^{18}O content of the oxidized products. These are calculated on an assumption that only the oxide ions corresponding to bismuth molybdate in the

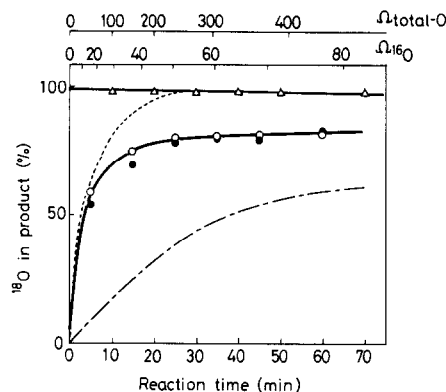


FIG. 4. Incorporation of ^{18}O into the oxidation products of propylene over $\text{Ba}_{11/12}\text{Bi}_{1/12}\text{MoO}_{4+x}$ catalyst. \circ , acrolein; \bullet , carbon dioxide; Δ , gaseous oxygen. (---) Theoretical curve calculated on the assumption that only lattice oxide ions in the hypothetical $\text{Bi}_2(\text{MoO}_4)_3$ phase are in rapid equilibrium with active species of oxygen. (- · -) Theoretical curve calculated on the assumption that lattice oxide ions in all catalyst particles are in rapid equilibrium with active species of oxygen.

catalysts are mobile and in rapid equilibrium with active species on the catalyst surface. In practice, much larger amounts of ^{16}O than expected in the above hypothesis were incorporated into the oxidation products; thus it is clear that lattice oxide ions not only in bismuth molybdate but also in other metal molybdates participate in the oxidation. Chain lines in the figures are also hypothetical; they show the time courses of the ^{18}O concentrations of the products under the complete mixing of all lattice oxide ions in the catalysts with active species of oxygen. The actual change observed in the experiment varies between the two hypothetical lines. In the case of the Pb-Bi-Mo-O system, the observed changes of the ^{18}O content in the oxidized products lie rather close to the chain lines. Considering diffusion of the lattice oxide ion to the surface, it seems reasonable to conclude that all lattice oxide ions in the catalyst particles can participate in the oxidation and exert some influence on the activity of the surface species of oxygen. Almost the same results were obtained for other scheelite-type cata-

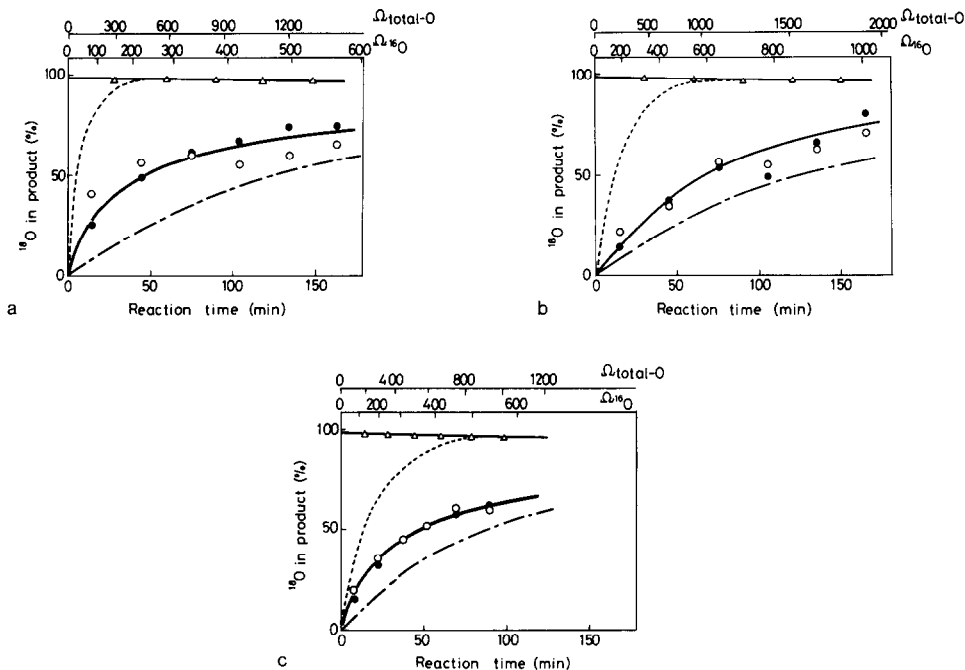


FIG. 5. Incorporation of ^{18}O into the oxidation products of propylene over Pb-Bi-Mo-O systems. \circ , acrolein; \bullet , carbon dioxide; Δ , gaseous oxygen. The two broken curves have the same meanings as those in Fig. 4, respectively. (a) $\text{Pb}_{29/30}\text{Bi}_{1/30}\text{MoO}_{4+x}$. (b) $\text{Pb}_{11/12}\text{Bi}_{1/12}\text{MoO}_{4+x}$. (c) $\text{Pb}_{7/8}\text{Bi}_{1/8}\text{MoO}_{4+x}$.

lysts, such as $\text{Ba}_{11/12}\text{Bi}_{1/12}\text{MoO}_{4+x}$ and $\text{Sr}_{11/12}\text{Bi}_{1/12}\text{MoO}_{4+x}$ which were examined in this experiment.

The catalytic behavior of these ternary-component oxides having scheelite-type structure was studied extensively by Aykan *et al.* and Sleight in the allylic oxidation of propylene (10, 11). They suggested that point defects in the form of cation vacancies (ϕ) were introduced by addition of bismuth cation into molybdates having the scheelite-type crystal structure of the form $\text{M}_{1-3x}^{2+}\text{Bi}_{2x}^{3+}\phi_x\text{MoO}_4$; the catalytic activity for these systems depends on the concentration of such cation vacancies. The addition of a small amount of bismuth ($x = 0.01$) remarkably improves the catalytic activity and also the selectivity of originally inactive MMoO_4 . Ternary-component oxides M-Bi-Mo-O having higher concentration of bismuth ($x > 0.03$) are also sufficiently active and selective for both

oxidation and ammoxidation of propylene. The present results are in good accordance with those reported by Aykan *et al.* As shown in Fig. 5, participation of lattice oxide ions in the oxidation was investigated for three Pb-Bi-Mo-O systems having different concentrations of bismuth. All these catalysts have a sufficient amount of bismuth and all show excellent catalytic activity and selectivity. Participation of the lattice oxide ions in the oxidation was extended to whole catalyst particles by the addition of bismuth molybdate to PbMoO_4 . The improvement of the catalytic activity of these catalysts seems just to correspond to the increase of the participation of the lattice oxide ions in the oxidation. Thus, one of the main roles of the cation vacancies seems to be to accelerate the diffusion of the bulk oxide ions and to maintain a higher activity of oxygen on the catalyst surface.

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