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PROMOTION EFFECT OF IRON FOR THE MULTICOMPONENT BISMUTH MOLYBDATE CATALYSTS AS REVEALED BY $^{18}O_2$ TRACER

Wataru UEDA, Yoshihiko MORO-OKA*, Tsuneo IKAWA, and Ikuya MATSUURA†

Research Laboratory of Resources Utilization, Tokyo Institute
of Technology, Nagatsuta-cho 4259, Midoriku, Yokohama 227
† The Universite Catholique de Louvain, Place Croix de Sud 1,
1348 Louvain-la-neuve, Belgium

Promotion effect of trivalent metal ions in tetra-component bismuth molybdate catalysts, $Mo_{12}Bi_1Co_8M^{III}_3O_x$ was investigated using $^{18}O_2$ tracer in the selective oxidation of propylene to acrolein. M^{III}, especially Fe^{3+}, introduces cation vacancies into $CoMoO_4$ in the form of $Co^{2+}_{1-3x}M^{III}_{2x}\phi_xMoO_4$ which accelerate the bulk diffusion of the lattice oxide ions to increase the catalytic activity of the multicomponent systems.

The multicomponent bismuth molybdate catalysts have been known as the most active and selective catalysts for the allylic oxidation of lower olefins. However, because of their complicated compositions, little has been reported for the role of each component in the catalyst systems. In this communication, we report a clear evidence that trivalent metal ions, especially Fe^{3+}, accelerate the bulk diffusion of the lattice oxide ions in the $M^{II}MoO_4$ phase to increase catalytic activity according to the Mars and van Klevelen mechanism.

Catalytic activity and selectivity for the oxidation of propylene to acrolein were determined using the conventional flow microreactor under an atmospheric pressure (Propylene; 16%, oxygen; 16%, nitrogen; balance). $^{18}O_2$ tracer experiments were carried out using the closed circulating system at 450°C under a reduced pressure (Propylene; 70 torr, $^{18}O_2$; 70 torr). Details of all experimental procedure and analytical method were the same as reported previously.[1-4)]

Multicomponent bismuth molybdate catalysts, $Mo_{12}Bi_1Co_8M^{III}_3O_x$ containing iron, chromium, or aluminum as the trivalent ion were prepared from the corresponding metal nitrate solutions and molybdic acid by the method reported by Wolfs and Batist.[5)] Characterization of the multicomponent catalysts are summarized in the table.

The specific activity to form acrolein of each catalyst tested is plotted against the temperature in Fig. 1. Summarizing the results obtained in this work and reported previously, the following tendencies are prominent.

1) In terms of specific activity, the pure bismuth molybdate, $Bi_2(MoO_4)_3$ is fairly active. However, owing to its low surface area, the activity per weight of the catalyst is not so high.

Table. Characterization of multicomponent bismuth molybdate catalysts

Catalyst	Phase detected by X-ray	Surface area (m^2/g)	Oxidation of propylene (450°C)		
			Rate x 10^5 (mol/min·m^2)	(mol/min·g)	Selectivity (%)
$Mo_3Bi_2O_{12}$	$Bi_2(MoO_4)_3$	1.8	9.7	17.5	93
$Mo_{12}Bi_1Co_{11}O_x$	β-$CoMoO_4$, $Bi_2(MoO_4)_3$	3.8	2.5	9.5	97
$Mo_{12}Bi_1Co_8Ni_3O_x$	β-$CoMoO_4$, $Bi_2(MoO_4)_3$	6.5	0.7	4.6	97
$Mo_{12}Bi_1Co_8Fe_3O_x$	β-$CoMoO_4$, $Bi_2(MoO_4)_3$, $Fe_2(MoO_4)_3$, $FeMoO_4$	7.1	30.8	218.7	96
$Mo_{12}Bi_1Co_8Cr_3O_x$	β-$CoMoO_4$, $Bi_2(MoO_4)_3$, $Cr_2(MoO_4)_3$	5.8	6.4	37.1	96
$Mo_{12}Bi_1Co_8Al_3O_x$	β-$CoMoO_4$, $Bi_2(MoO_4)_3$, $Al_2(MoO_4)_3$	8.5	5.1	43.4	95

2) The specific activity of tri-component system, $Mo_{12}Bi_1M^{II}_{11}O_x$ does not exceed that of the pure bismuth molybdate.

3) Replacement of a part of the third component, M^{II} in the $Mo_{12}Bi_1M^{II}_{11}O_x$ by a trivalent ion increases the specific activity of the catalyst system. Although aluminum or chromium is effective to some extent, iron increases the specific activity most effectively with excellent selectivity to acrolein as claimed in many patents.

4) On the contrary, replacement of M^{II} by another divalent ion instead of trivalent ion is not effective for improving the specific activity.

Incorporation of the lattice oxide ions into the oxidized products was examined in the oxidation of propylene with $^{18}O_2$ (99.1%) on the $Mo_{12}Bi_1Co_8Fe_3O_x$ catalyst. The results are shown in Fig. 2, where $\Omega_{total\text{-}O}$ and $\Omega_{^{16}O}$ denote the total amount of oxygen consumed in the oxidation and the total amount of the lattice oxide ion incorporated into the oxidized products expressed as the unit of oxide ion layer of the catalyst used with assuming 1 x 10^{19} oxygen ion/surface area (m^2). As clearly shown in the figure, the oxidation proceeds via the Mars and van Klevelen mechanism. It has been reported and is also confirmed by X-ray analysis in the present work that the multicomponent bismuth molybdate catalysts are composed of multiphase of different

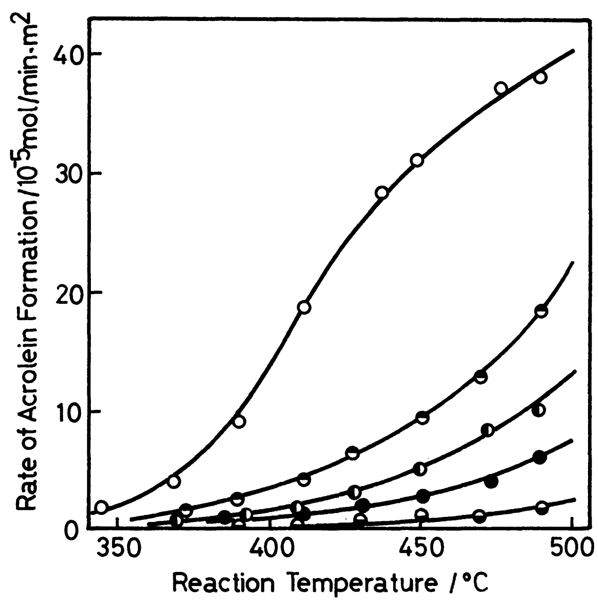

Figure 1. Specific activity of multicomponent bismuth molybdate catalysts in the oxidation of propylene to acrolein.

◓ , $Mo_3Bi_2O_{12}$; ● , $Mo_{12}Bi_1Co_{11}O_x$;
◒ , $Mo_{12}Bi_1Co_8Ni_3O_x$; ○ , $Mo_{12}Bi_1Co_8Fe_3O_x$;
◐ , $Mo_{12}Bi_1Co_8Al_3O_x$.

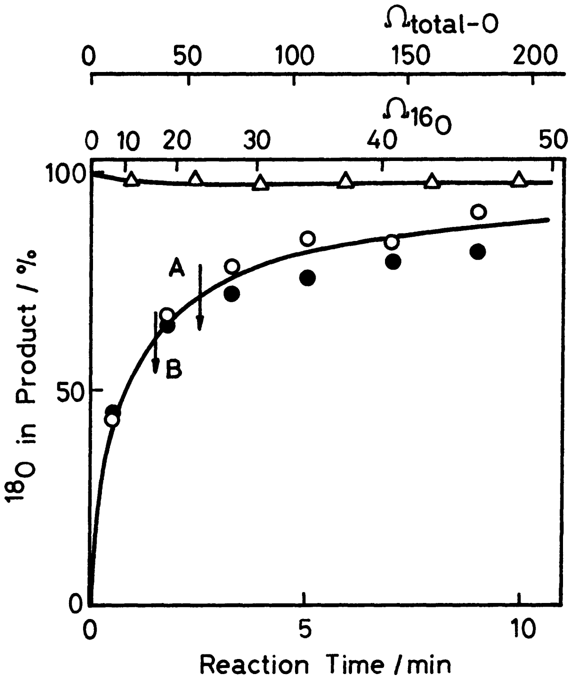

Figure 2. ^{18}O Concentration of the oxidation products of propylene with $^{18}O_2$ over $Mo_{12}Bi_1Co_8Fe_3O_x$ catalyst.

○ , acrolein; ● , carbon dioxide; △ , gaseous oxygen.

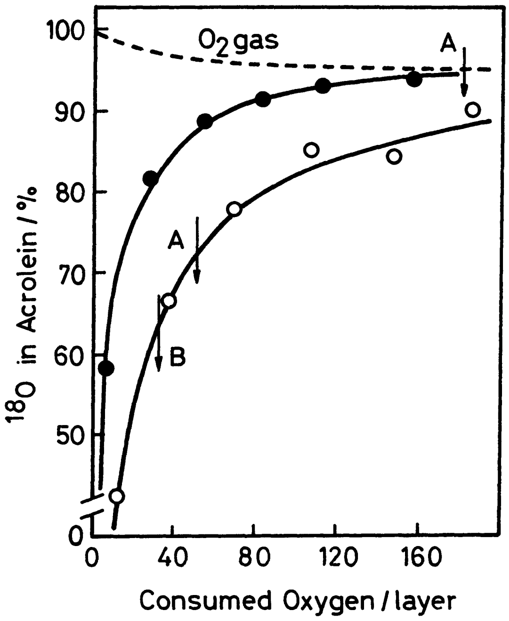

Figure 3. ^{18}O Concentration of acrolein as a function of the consumed oxygen per unit surface area of the catalysts, $\Omega_{total\text{-}O}$.

● , $Mo_{12}Bi_1Co_{11}O_x$;
○ , $Mo_{12}Bi_1Co_8Fe_3O_x$.

metal molybdates and bismuth molybdate phase is liable to be condensed on the surface of the catalyst particles.[5-7] The arrow mark (A) in the figure shows a point where the amount of ^{16}O incorporated into the oxidized products from the catalyst reaches the same amount as oxide ions in the bismuth molybdate phase in the catalyst. The arrow mark (B) indicates the point where $^{16}O^{2-}$ of a composite oxide ($Bi_3FeMo_2O_{12}$) reported by Keulks[8] and Sleight[9], if it exists, is consumed. The lattice oxide ions are available to the reaction far beyond these two points. This result is quite different from that obtained on the tri-component catalyst systems, $Mo_{12}Bi_1M^{II}_{11}O_x$ reported previously.[3]

In order to compare the degree of the participation of the lattice oxide ions in the reaction for tri- and tetra-component systems, ^{18}O concentrations of acrolein obtained in the oxidation on the $Mo_{12}Bi_1Co_{11}O_x$ as well as the $Mo_{12}Bi_1Co_8Fe_3O_x$ are plotted against $\Omega_{total\text{-}O}$ in Fig. 3. In the case of the tri-component catalyst, the ^{18}O concentration in acrolein reaches the same value as that of gaseous oxygen at the point indicated by the arrow mark (A). This shows that all $^{16}O^{2-}$ of the bismuth molybdate phase are replaced by $^{18}O^{2-}$ at this stage and only lattice oxide ion in bismuth molybdate phase are active for the reaction. On the contrary, in the case of the $Mo_{12}Bi_1Co_8Fe_3O_x$ catalyst, it is clear that the lattice oxide ions not only in the bismuth molybdate phase but also in the other transition metal molybdates are active and participate in the reaction.

The effect of the component element on the activity of the lattice oxide ions is further exemplified in Fig. 4 by the similar plots for $Mo_{12}Bi_1Co_8Cr_3O_x$,

$Mo_{12}Bi_1Co_8Al_3O_x$, and $Mo_{12}Bi_1Co_8Ni_3O_x$ in addition to the catalysts shown in Fig. 3. It is clearly demonstrated that the replacement of Co^{2+} in $Mo_{12}Bi_1Co_{11}O_x$ by the trivalent ions makes the lattice oxide ions in the transition metal molybdates active but the replacement by the divalent ion, Ni^{2+}, is not effective. These effects seem to just correspond to the specific activity of the multi-component system.

The promotion effect of iron in the oxidation catalyst has been often attributed to the lower redox potential of $Fe^{3+} + e \rightleftharpoons Fe^{2+}$. However, this is not applicable to the present system, because Cr^{3+} or Al^{3+} is also effective to improve the catalytic activity. Sleight et al suggested that point defects in the form of $Pb^{2+}_{1-3x}Bi^{3+}_{2x}\phi_xMoO_4$ (ϕ; cation vacancy) were introduced by addition of bismuth cation into $PbMoO_4$ and the catalytic activity of these systems depends on the concentration of such vacancies.[10] Our results obtained in this investigation strongly suggest that the vacancies of the same type as $Co^{2+}_{1-3x}M^{III}_{2x}\phi_xMoO_4$ are formed in $CoMoO_4$ by the trivalent cations and these vacancies accelerate the bulk diffusion of the lattice oxide ions. At this stage, it is not clear whether this acceleration increases the number of the active sites or lowers the activation energy of the reaction. Determination of the accurate kinetic factors and reduction and reoxidation experiments of the catalysts are underway to clarify the problem.

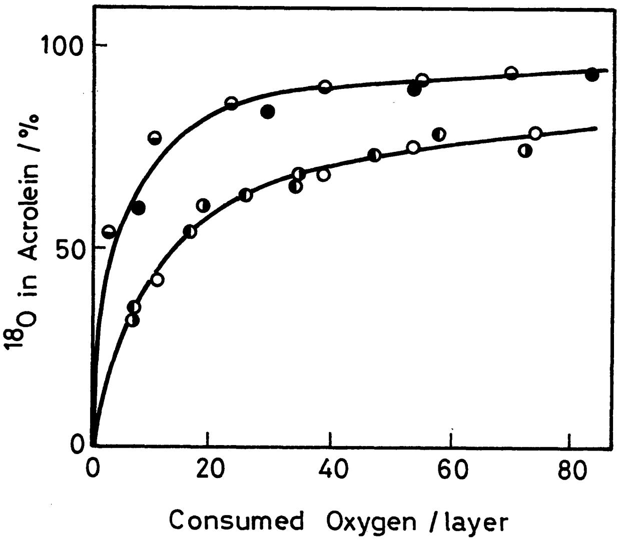

Figure 4. ^{18}O Concentration of acrolein as a function of the consumed oxygen per unit surface area of the catalysts, $\Omega_{total-O}$.

● , $Mo_{12}Bi_1Co_{11}O_x$; ⊖ , $Mo_{12}Bi_1Co_8Ni_3O_x$;
○ , $Mo_{12}Bi_1Co_8Fe_3O_x$; ◑ , $Mo_{12}Bi_1Co_8Cr_3O_x$;
◐ , $Mo_{12}Bi_1Co_8Al_3O_x$.

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