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Promotion effect of molybdate support on $Bi_2Mo_3O_{12}$ catalyst in the selective oxidation of propylene

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Catalytic behavior of $Bi_2Mo_3O_{12}$ supported on $CoMoO_4$ or $CO_{11/12}Fe_{1/12}MoO_x$ was investigated in the oxidation of propylene to acrolein. A drastic promotion effect was observed only in the catalyst supported on $Co_{11/12}Fe_{1/12}MoO_x$ but not on $CoMoO_4$. Promotion effect of cobalt and iron in the multicomponent bismuth molybdate catalyst, Mo-Bi-M^{II}-M^{III}-O was discussed.

Keywords: Catalytic oxidation; propylene; acrolein; supported $Bi_2Mo_3O_{12}$

1. Introduction

Composite oxides between bismuth and molybdenum have been widely used for the catalytic oxidation and ammoxidation of propylene, since the initial discovery of the reactions in 1959 [1]. Both reactions have been improved industrially year by year, and finally established by the use of quite complicated mixed metal oxide catalysts, the so-called multicomponent bismuth molybdate catalysts. Although the reaction mechanisms over bismuth molybdates have been elucidated [2], it is still not clear why the multicomponent bismuth molybdate catalysts are much active and selective compared to the simple bismuth molybdates. Owing to their complicated compositions and structures [3–10], little has been reported for the working mechanism and the role of each component in the catalyst systems.

Multicomponent bismuth molybdate catalysts claimed in recent patents include a number of elements in addition to molybdenum and bismuth. The

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general formula of them may be described as follows;

$\boxed{\text{Mo-Bi-M}^{II}\text{-M}^{III}}\text{-M}^{I}\text{-X-Y-O}$ M^{II}: CO, Ni, Mn, Mg, (Pb),....
Fundamental structure M^{III}: Fe, Cr, Ce, Al,...especially Fe.
M^{I}: Na, K, Cs, Tl,....
X: Sb, Te, W, V, Nb,....
Y: P, B,....

The first four elements are essential and consist of a fundamental structure of the catalyst systems, and the remains are usually added for the enhancement of catalyst life and mechanical strength and the minor improvements of the catalytic activity and selectivity. The role of alkali metal is very important to complete the industrial oxidation catalyst. However, the catalyst system becomes too complicated when all necessary elements are included. Thus, the investigation of our group has been directed to the working mechanism of the fundamental structure, Mo-Bi-M^{II}-M^{III}-O.

It is generally accepted that bismuth molybdates are located on the surface of the catalyst particle and work as main active species in the catalyst systems [5]. On the other hand, $M^{II}MoO_4$ and $M_2^{III}(MoO_4)_3$ are concentrated in the bulk of the catalyst particle and serve as a support for the active components. However, the catalyst system shows excellent activity only when it includes both M^{II} and M^{III} having almost same ionic radii besides of bismuth and molybdenum. It was found that the catalyst system, Mo-Bi-M^{II}-O or Mo-Bi-M^{II}-M'^{II}-O never exhibits high activity for the oxidation of propylene [11–13].

To clarify the role of M^{II} and M^{III} additives in the catalyst system, the catalytic activity was examined for the bismuth molybdate supported on metal molybdates in various loading amounts. This letter describes the importance of strong interaction between the catalyst oxide and the support oxide to prepare highly functionalized active catalyst systems. The roles of the M^{II} and M^{III} additives are reasonably explained on the basis of the experimental results obtained in the propylene oxidation to acrolein over $Bi_2Mo_3O_{12}$ catalysts supported on $CoMoO_4$ and $Co(Fe)MoO_x$.

2. Preparation and characterization of the catalysts

PREPARATION OF $Bi_2Mo_3O_{12}$ CATALYSTS SUPPORTED ON $CoMoO_4$ AND $Co_{11/12}Fe_{1/12}MoO_x$

$CoMoO_4$ was prepared by the usual coprecipitation method from a cobalt nitrate solution and an ammonium molybdate solution, followed by the calcination in air at 500°C for 20 h [3]. $Co_{11/12}Fe_{1/12}MoO_x$ was prepared by the solid state reaction between cobalt oxalate and ferrous oxalate at 520°C for 40 h.

$CoMoO_4$ and $Co_{11/12}Fe_{1/12}MoO_x$ has the surface area of 14.3 and 11.5 m^2/g, respectively. $Bi_2Mo_3O_{12}$ was supported on both molybdates in various loading amounts, e.g., $Bi_2Mo_3O_{12}/Co_{11/12}MoO_x$ from 0 to 0.3. Co(Fe)MoO_x powder was first impregnated with an ammonium molybdate solution. After drying by evaporation, it was again impregnated with an acetone solution of triphenyl bismuth. The mixture was dried by evaporation and then calcined in air at 500°C for 2 h.

CHARACTERIZATION

The bismuth molybdate catalysts supported on $CoMoO_4$ or $Co_{11/12}Fe_{1/12}$ MoO_x were characterized by XRD, TEM, EDX, ESR, and BET measurements. XRD peaks of $Bi_2Mo_3O_{12}$ and $CoMoO_4$ phases were observed in every catalyst prepared. Neither bismuth molybdates other than $Bi_2Mo_3O_{12}$ nor any composite oxides among Mo, Bi, Co, and Fe were detected. It is clear that almost all iron cations in $Co_{11/12}Fe_{1/12}MoO_x$ were completely dissolved in the $CoMoO_4$ matrix as a solid solution.

It is noteworthy that clear XRD patterns for $Bi_2Mo_3O_{12}$ were observed only when the molar ratio of supported $Bi_2Mo_3O_{12}$ to Co(Fe)MoO_x was higher than 0.005 which corresponds to monolayer coverage of the supports by $Bi_2Mo_3O_{12}$. The XRD peak height ratios of d_{221} of $Bi_2Mo_3O_{12}$ to d_{220} of Co(Fe)MoO_x are plotted against the loading amount of $Bi_2Mo_3O_{12}$ in fig. 1. The peak intensity ratios d_{221}/d_{220} of the mechanical mixtures of $Bi_2Mo_3O_{12}$ and Co(Fe)MoO_x are also plotted in this figure. The ratio of d_{221}/d_{220} increases linearly with increasing the molar ratio of $Bi_2Mo_2O_{12}$ to Co(Fe)MoO_x in the same manner for both series of the catalysts. The observed same inclination suggests that $Bi_2Mo_3O_{12}$ crystals grew with the increasing concentration of loaded bismuth and molybdenum after the surface of the supports was covered with the monolayer of $Bi_2Mo_3O_{12}$.

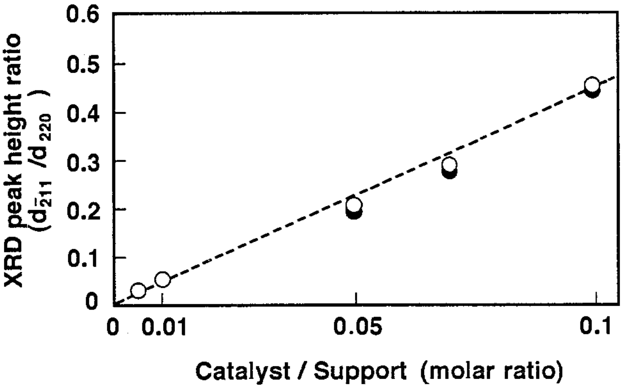

Fig. 1. Variation of XRD peak height ratio with the loading amount of $Bi_2Mo_3O_{12}$ on two metal molybdates: ● $Bi_2Mo_3O_{12}/Co_{11/12}Fe_{1/12}MoO_x$; ○ $Bi_2Mo_3O_{12}/CoMoO_4$. The broken line is for the mechanical mixtures of $Bi_2Mo_3O_{12}$ and $CoMoO_4$.

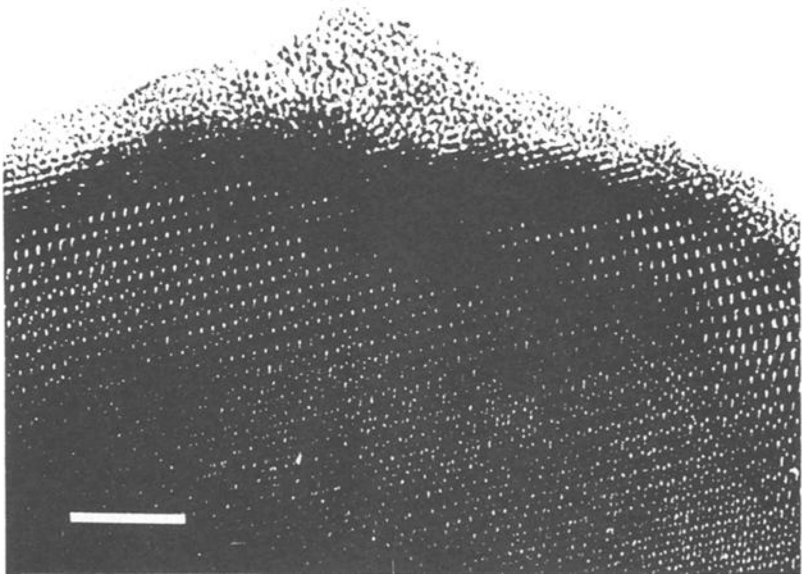

Fig. 2. High-resolution electron microscope image of $Bi_2Mo_3O_{12}/Co_{11/12}Fe_{1/12}MoO_x$. The scale bar corresponds to 100 Å.

This was further confirmed by the TEM measurement and the X-ray emission analysis. Typical results for a specimen with a composition of $Bi_2Mo_3O_{12}/Co_{11/12}Fe_{1/12}MoO_x$ (0.1) are shown in figs. 2 and 3. Fig. 2 shows a high

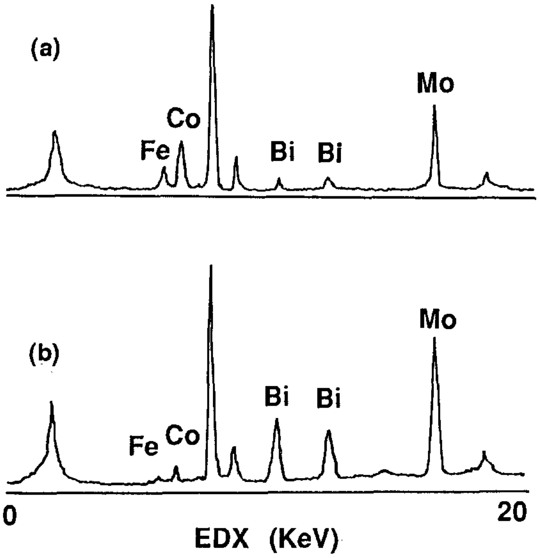

Fig. 3. EDX analysis of $Bi_2Mo_3O_{12}/Co_{11/12}Fe_{1/12}MoO_x$. The analysis was carried out at the middle (a) and edge (b) point of the crystal.

Table 1
Catalyst composition and surface area

Catalyst composition [a]	Surface area (m^2/g) of	
	$Bi_2Mo_3O_{12}$ / $Co_{11/12}Fe_{1/12}MoO_x$	$Bi_2Mo_3O_{12}$ / $CoMoO_4$
$CoMoO_4$	14.3	–
$Co_{11/12}Fe_{1/12}MoO_x$	–	11.5
0.0001	13.8	9.8
0.0005	13.7	7.5
0.001	13.2	6.7
0.002	10.1	6.4
0.005	4.8	5.3
0.01	4.5	3.4
0.03	3.2	3.0
0.05	2.7	2.8
0.1	2.6	2.0
0.3	1.4	1.4
$Bi_2Mo_3O_{12}$	2.1	

[a] Molar ratio of $Bi_2Mo_3O_{12}$ to support molybdate.

resolution electron micrograph (HREM) image of the crystal. The specimen is biphasic, one main phase being identified as $CoMoO_4$ structure and the other as $Bi_2Mo_3O_{12}$. The HREM image shows the presence of an additional distinct phase located on the surface of $CoMoO_4$ crystal. Although no clear lattice image was observed on this portion, the phase could be identified as $Bi_2Mo_3O_{12}$ by the comparison of the X-ray emission spectra at the edge portion of the crystal and at the inner portion in fig. 3. Since the HREM image of the main phase shows no severe disorder in the lattice, the supported bismuth molybdenum elements may dominantly locate on the surface of the crystal with $CoMoO_4$ structure, forming thin layers and then small crystals of $Bi_2Mo_3O_{12}$ attached on the main structure.

Lastly, the oxidation state of iron in $Co_{11/12}Fe_{1/12}MoO_x$ was examined by ESR measurement. It was found that iron mainly existed as a divalent cation but part of it acted as a trivalent one. The catalyst compositions and their surface areas are summarized in table 1.

3. Propylene oxidation on supported $Bi_2Mo_3O_{12}$ catalysts

Catalytic activities of the $Bi_2Mo_3O_{12}$ supported on the metal molybdates, $CoMoO_4$ and $Co_{11/12}Fe_{1/12}MoO_x$, were examined in the oxidation of propylene to acrolein using a conventional flow reactor. The reaction was carried out with 1 g of the catalyst powder diluted by 5 g of quartz tips. Reaction gas mixture

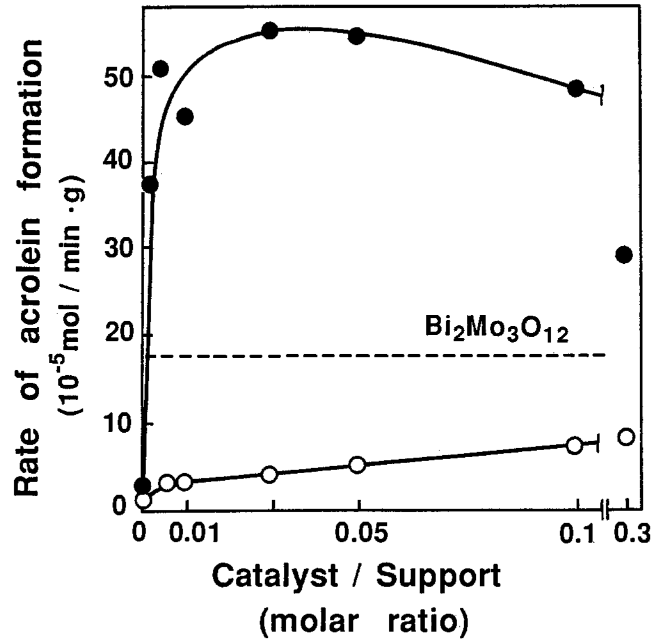

Fig. 4. Catalytic activities per unit weight of the supported bismuth molybdate catalysts: ● $Bi_2Mo_3O_{12}/Co_{11/12}Fe_{1/12}MoO_x$; ○ $Bi_2Mo_3O_{12}/CoMoO_4$ in the oxidation of propylene at 450°C.

under an atmospheric pressure (propylene 16.7%, O_2 16.7%, N_2 balance) was made to flow at the rate of 120 $ml.min^{-1}$ at 450°C.

Drastic effects of the supports on the activity and selectivity of $Bi_2Mo_3O_{12}$ in the propylene oxidation are demonstrated in figs. 4, 5, and 6. Different from

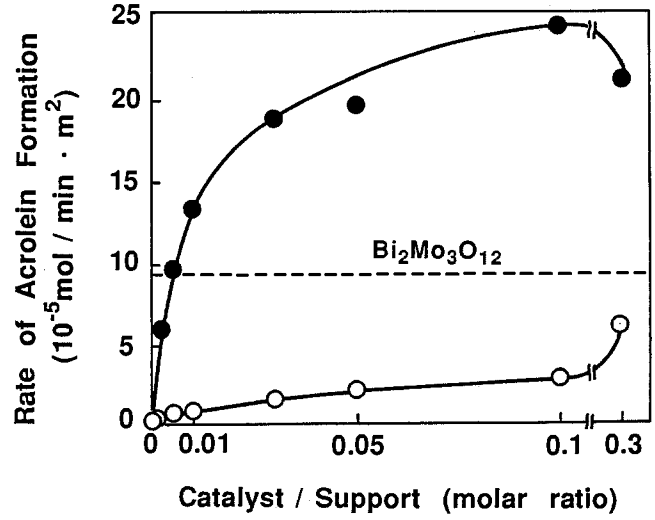

Fig. 5. Specific activities of the supported bismuth molybdate catalysts: ● $Bi_2Mo_3O_{12}/Co_{11/12}Fe_{1/12}MoO_x$; ○ $Bi_2Mo_3O_{12}/CoMoO_4$ in the oxidation of propylene at 450°C.

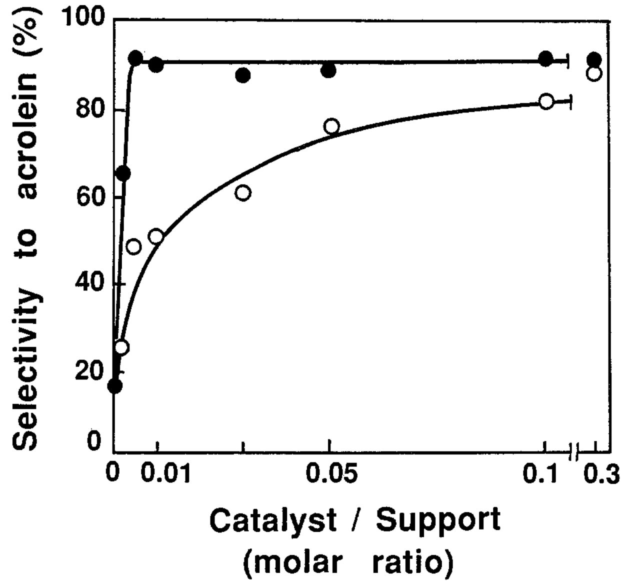

Fig. 6. The selectivity to acrolein in the oxidation of propylene on the supported bismuth molybdate catalysts: ● $Bi_2Mo_3O_{12}/Co_{11/12}Fe_{1/12}MoO_x$; ○ $Bi_2Mo_3O_{12}/CoMoO_4$.

bismuth molybdates, either $CoMoO_4$ or $Co_{11/12}Fe_{1/12}MoO_x$ showed quite lower activity to form acrolein. These support molybdates mainly gave carbon oxides under the conditions adopted in these experiments. However, the addition of small amounts of $Bi_2Mo_3O_{12}$ to $Co_{11/12}Fe_{1/12}MoO_x$ gave dramatic improvements both in the catalytic activity and selectivity. The formation of carbon oxides was suppressed remarkably and the selectivity to acrolein reached 90% of the converted propylene. The catalytic activity of $Bi_2Mo_3O_{12}/Co_{11/12}Fe_{1/12}$ MoO_x also increases steeply with increasing loading amount of $Bi_2Mo_3O_{12}$ as shown in figs. 4 and 5. When the molar ratio of the catalyst to the support reached the value of 0.005 corresponding to a monolayer coverage of $Bi_2Mo_3O_{12}$ on the $Co_{11/12}Fe_{1/12}Fe_{1/12}MoO_x$ surface, the catalyst showed almost comparable specific activity to that of pure $Bi_2Mo_3O_{12}$. Since the support has a larger specific surface area than pure $Bi_2Mo_3O_{12}$, the activity per unit weight exceeds far beyond that of pure $Bi_2Mo_3O_{12}$.

The catalytic activity of the $Bi_2Mo_3O_{12}/Co_{11/12}Fe_{1/12}MoO_x$ increases further with increasing the loading amount of $Bi_2Mo_3O_{12}$. Both the specific activity (activity per unit surface area) and the activity per unit weight of the catalyst reach much higher values than those of the pure $Bi_2Mo_3O_{12}$. Too much addition of the bismuth molybdate decreases the catalytic activity per unit weight of the catalyst, since the specific surface area of the catalyst system decreases with the loading amount of $Bi_2Mo_3O_{12}$. The specific activity is also decreased by higher loading of $Bi_2Mo_3O_{12}$ as shown in fig. 6. Thus, it is clear that $Co_{11/12}Fe_{1/12}MoO_x$ is not a simple support for the active component but

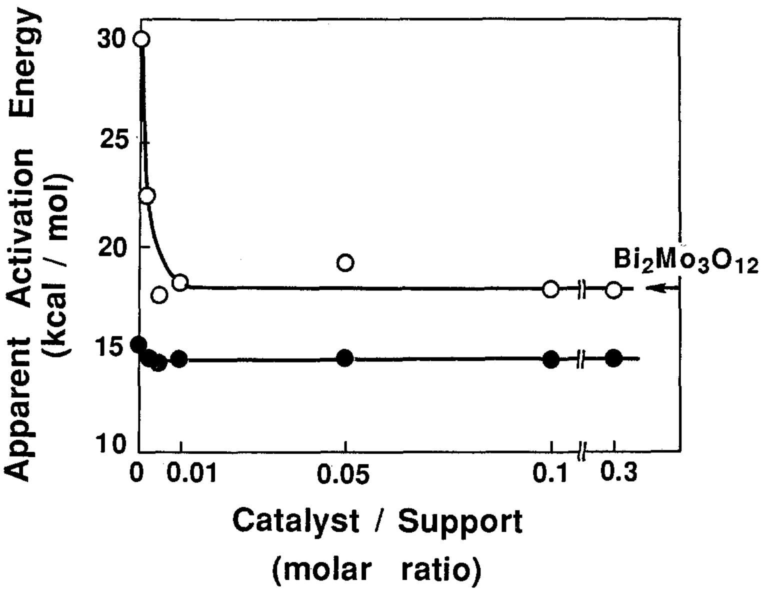

Fig. 7. The apparent activation energy of the reaction on the supported bismuth molybdate catalyst: ● $Bi_2Mo_3O_{12}/Co_{11/12}Fe_{1/12}MoO_x$; ○ $Bi_2Mo_3O_{12}/CoMoO_4$.

would give the same direct effect on the acrolein formation other than the enlargement of the surface area of $Bi_2Mo_3O_{12}$.

On the contrary, the catalytic activity of the $Bi_2Mo_3O_{12}/CoMoO_4$ system increases quite slowly with the loading amount of $Bi_2Mo_3O_{12}$ and never exceeds that of pure $Bi_2Mo_3O_{12}$. Improvement of the selectivity to acrolein was also poor.

The prominent difference in the catalytic activity depending on the type of the support molybdate is reflected in the apparent activation energies as shown in fig. 7. The apparent activation energy of $Bi_2Mo_3O_{12}/Co_{11/12}Fe_{1/12}MoO_x$ system shows a minor change with the loading amount of the bismuth molybdate and is lower than that of the pure $Bi_2Mo_3O_{12}$ by 3 kcal mol. On the other hand, the apparent activation energy of the $Bi_2Mo_3O_{12}/CoMoO_4$ system varies considerably with the loading amount of $Bi_2Mo_3O_{12}$ and finally coincides with that of the pure $Bi_2Mo_3O_{12}$ at higher loadings.

4. Discussion

The results mentioned above clearly show that the oxidation of propylene to acrolein proceeds on the pure $Bi_2Mo_3O_{12}$ crystals in the $Bi_2Mo_3O_{12}/CoMoO_4$ system and $CoMoO_4$ serves as simple supports for the active component. However, the situation is fairly different from that in the catalysts supported on the cobalt molybdate containing iron. Since the catalyst surface is mostly covered with the bismuth molybdate, it is sure that the reaction proceeds on the $Bi_2Mo_3O_{12}$. It has been estimated that the $Bi_2Mo_3O_{12}$ supported on the $Co_{11/12}Fe_{1/12}MoO_x$ is considerably modified by the support molybdate and there exists some strong interaction between the bismuth molybdate catalyst and the support molybdate.

It is noteworthy that the results obtained in this investigation correspond to the tendency observed in the activity tests for the tri- and tetra-component bismuth molybdate catalysts. It was demonstrated that the multicomponent bismuth molybdate is active only when the catalyst system includes divalent Co^{2+} and trivalent Fe^{3+} simultaneously [11–13]. It is well-known that Co^{2+} and Fe^{3+} activate molecular oxygen more effectively than bismuth molybdates. Delmon and his coworkers suggested that the promotion effect of additional metal oxides to bismuth molybdate may be attributed to the spillover of oxygen species activated on the additive oxides [14,15]. However, it is difficult to explain the drastic difference of the promotion effect between $CoMoO_4$ and $Co_{11/12}Fe_{1/12}MoO_x$ supports by their "remote control theory". In addition, surface migration of oxide ion on the oxide surface is not so easy under the conditions adopted in this investigation. Instead of the surface migration, bulk diffusion of oxide ion is rather possible when lattice vacancies exist in the oxide particle [16]. We have found that lattice oxide ions not only in the bismuth molybdate phase but also in other transition metal molybdates are involved in the reaction in the Mo-Bi-Co^{2+}-Fe^{3+}-O systems according to the Mars and Van Krevelen mechanism while lattice oxide ions only in bismuth molybdates phase take part in the reaction in the Mo-Bi-Co^{2+}-O system [13]. A part of iron evidently exists as Fe^{3+} in the $Co_{11/12}Fe_{1/12}MoO_x$ support where lattice vacancies inevitably formed to compensate excess charge of the trivalent cation in the $CoMoO_4$ matrix. Although the most part of the catalyst is covered with $Bi_2Mo_3O_{12}$, small amounts of cobalt and iron are found in the surface layer of the catalyst by XPS analysis [5]. We conclude that the prominent promotion effect of the $Co_{11/12}Fe_{1/12}MoO_x$ support to the bismuth molybdate catalyst may be attributable to the migration of active oxygen species from cobalt or iron molybdate to Bi_2Mo_{O12} by the bulk diffusion through lattice vacancies in the support molybdate. Further evidence for this conclusion will be shown by ^{18}O tracer investigations in following papers.

References

[1] J.D. Idol, Jr., (Standard Oil Co.) USP 2,904,580 (1959).

[2] J.D. Burrington, C.T. Kartisek and R.K. Grasselli, J. Catal. 63 (1980) 235; 75 (1982) 225; 81 (1983) 489; 83 (1984) 363.

[3] M.W.J. Wolfs and Ph.A. Batist, J. Catal. 32 (1974) 25.

[4] I. Matsuura and M.W.J. Wolfs 37 (1975) 174.

[5] I. Matsuura, *Proc. 7th Intern. Congr. Catal.* Tokyo, 1980, eds. T. Seiyama and K. Tanabe (Kodansha, Tokyo/Elsevier, Amsterdam, 1981) Part B, p. 1009.
[6] T.S.R. Prasada Rao and P.G. Menon, J. Catal. 51 (1978) 64.
[7] W.J.V. Ooij and W.J. Muizebelt, *Proc. Intern. Vac. Congr. & 3rd Intern. Conf. Solid Surf.*, Vienna 1977, p. 839.
[8] S. Umemura, K. Ohdan and H. Asada, *5th Soviet-Japan Catal. Seminar*, 1979, p. 60.
[9] O.V. Krylov, Kinet Katal. 25 (1984) 955.
[10] T.S.R. Prasada Rao and K.R. Krishnamurthy, J. Catal. 95 (1985) 209.
[11] Y. Moro-oka, W. Ueda, S. Tanaka and T. Ikawa, *7th Intern. Congr. Catal.*, Tokyo, 1980, eds. T. Seiyama and K. Tanabe (Kodansha, Tokyo/Elsevier, Amsterdam, 1981) Part B, p. 1086.
[12] W. Ueda, Y. Moro-oka and T. Ikawa, J. Catal. 70 (1981) 409.
[13] W. Ueda, Y. Moro-oka, T. Ikawa and I. Matsuura, Chem. Lett. (1982) 1365.
[14] J.M.D. Tascon, P. Graange and B. Delmon, J. Catal. 97 (1987) 287;
J.M.D. Tascon, P. Bertrand, M. Genet and B. Delmon, J. Catal. 97 (1986) 300;
J.M.D. Tascon, M.M. Mestdagh and B. Delmon, J. Catal. 97 (1986) 312.
[15] P. Ruiz, M. Zhou, T. Remy, F. Machej, F. Aoun and B. Delmon, Catal. Today 1 (1987) 181;
F.Y. Qui, L.T. Weng, P. Ruiz and B. Delmon, Appl. Catal. 47 (1989) 115;
L.T. Weng, S.Y. Ma, P. Ruiz and B. Delmon, J. Mol. Catal. 61 (1990) 99.
[16] W. Ueda, K. Asakawa, C.L. Chen, Y. Moro-oka and T. Ikawa, J. Catal. 101 (1986) 360;
W. Ueda, C.L. Chen, K. Asakawa, Y. Moro-oka and T. Ikawa, J. Catal. 101 (1986) 369.