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# Structure of Multicomponent Oxide Catalyst for Oxidative Butene Dehydrogenation

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Three samples of a catalyst with general formula $Mo_{12}Ni_{4.5}Co_4Fe_1Bi_1P_{0.08}Tl_{0-0.6}O_{47.7-48.0}Si_{15}$, which exhibits high activity and selectivity for oxidative butene dehydrogenation, have been studied by X-ray analysis, ESR, ir, and diffuse-reflectance spectroscopy. Molybdates of the elements represented in the composition are shown to be present. In the catalyst containing 0.6 atom fraction Tl, which displays the maximum activity and selectivity, changes in the structure have been established. It is found that part of $Mo^{6+}$ and $Fe^{3+}$ ions are reduced to a lower valence state in the deactivated catalyst samples.

## INTRODUCTION

A great number of oxide catalysts exhibit catalytic activity for partial olefinic oxidation. The catalysts used are very varied, and include the molybdates, phosphates and tungstates of Bi, Ca, Co, Fe, Mn, Ni, Sn–Sb oxides, and Fe–Mn oxides. Irrespective of the great diversity of catalysts, Bi molybdate is most frequently employed. It forms several phases, notably $\alpha$-$Bi_2Mo_3O_{12}$, $\beta$-$Bi_2Mo_2O_9$, and $\gamma$-$Bi_2MoO_6$. The comparison of their activities for 1-butene oxidation shows that $\gamma$-$Bi_2MoO_6$ calcined at 500°C displays the highest activity (*1*). Calcination at a higher temperature (680°C) strongly reduces its activity, probably owing to a lower specific surface. $\beta$-$Bi_2Mo_2O_9$ shows also a good activity, while $\alpha$-$Bi_2Mo_3O_{12}$ is less active. Batist *et al.* (*2*) examined the effect of a small amount of $BiPO_4$, $Fe_2(MoO_4)_3$, and $Cr_2(MoO_4)_3$ on $\alpha$-$Bi_2Mo_3O_{12}$ which as a free phase exhibits only a moderate activity for oxidative dehydrogenation of butene. According to these authors, the promoting effect of these additives is probably attributable to an inhibition of the $\alpha$-phase formation. They favor the formation of the $\gamma$-phase, which is more active, and its presence has been found by X-ray analysis when $BiPO_4$ and $Fe_2(MoO_4)_3$ are used as additives. This effect may be interpreted in terms of the relative preference of the trivalent cation for $O^{2-}$ or $(MoO_4)^{2-}$ resulting in a shift of the following equilibrium to the left or right:

$$Me_2^{3+}(MoO_4)_3^{2-} + (BiO)_2^{+}(MoO_4)^{2-} \rightleftarrows (MeO)_2^{+}(MoO_4)^{2-} + Bi_2^{3+}(MoO_4)_3^{2-}.$$

Moreover, the rate of electron transfer from the catalyst cations to the oxygen and the ability of the catalyst to dissociate oxygen from the gas phase are increased.

Most of the catalysts exhibiting high activity and selectivity used in industry are multicomponent systems. In view of their great industrial importance, their physicochemical and structural properties merit detailed study, in spite of the difficulties due to the complex composition.

## EXPERIMENTAL

The catalyst studied in this paper had a general formula $Mo_{12}Ni_{4.5}Co_4Fe_1Bi_1P_{0.08}Tl_{0-0.6}O_{47.7-48.0}Si_{15}$ and was produced in the Department of Catalysis of the Scientific Research Center of Sumitomo Chem. Ltd., Japan. It displays high activity and selectivity for oxidative dehydrogenation of butene to butadiene. It was prepared by coprecipitation of salts of the participating elements with silica gel. The resultant

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dispersion was evaporated to dryness and the residue was calcined at 300°C. After that it was cooled and crushed. The obtained powder was tableted and calcined again at 525°C.

Three samples differing in the content of thallium, i.e., 0, 0.3, and 0.6 atom fractions Tl, were studied as air-dried samples, as samples activated with steam and air at 350°C, and as samples used for dehydrogenation of butene in the absence of oxygen at the above temperature.

In order to study the nature of the changes in the catalyst as a result of the reaction, each sample was investigated by various physical methods before and after dehydrogenation of butene. The samples were placed in a quartz reaction vessel supplied with stopcocks at the entrance and exit side. The catalyst was activated with air and steam at 350°C. For the reaction studies the samples were heated in an air flow to the above temperature. Then the air was stopped and 1-butene pulses (1 ml) were passed in a flow of nitrogen. After each pulse a sample was taken from the reaction mixture and analyzed by a gas chromatograph. The *cis*- and *trans*-2-butene and butadiene were obtained as reaction products. The butene conversion and butadiene yield decreased with successive pulses and when only traces of butadiene were left, the ESR spectrum of the catalyst sample was recorded. It was compared with that recorded after activation and that recorded before the reaction.

ESR spectra were obtained using a 3BS-X Jeol apparatus at room temperature using $Mn^{2+}$ ions as a standard, not allowing air access to the spent catalyst. X-Ray analysis of the catalyst was carried out using a Philips diffractometer with Co$K\alpha$ radiation. Diffuse-reflectance spectra were recorded by use of a Beckman 5270 spectrophotometer equipped with a reflectance sphere, with $BaSO_4$ as a standard of comparison in a quartz vessel evacuated to $4 \times 10^{-3}$ Torr pressure. For ir spectra the catalyst samples were pressed into CsI disks and spectra were obtained with a Perkin–Elmer 180 spectrophotometer. Electron micrographs were obtained in conditions of secondary electrons and the distribution of components was studied by an X-ray microanalyzer XMA-733. Differential thermal analysis and thermogravimetric analysis were made in an air atmosphere from 20 to 1000°C using a Derivatograph MOM Type 3427.

## RESULTS AND DISCUSSION

X-Ray analysis showed that the molybdates of the elements represented in the catalyst composition were present. Comparisons were made with the interplanar spacings of the separate phases taken from the Powder Diffraction File (*3*). Bi molybdate was present as a mixture of two phases: $\alpha$-$Bi_2Mo_3O_{12}$ and $\gamma$-$Bi_2MoO_6$. Bivalent and trivalent Fe ions were found as $FeMoO_4$ and $Fe_2(MoO_4)_3$. Evidence for the presence of the crystalline hydrates of nickel and cobalt molybdates was also obtained and a small amount of free $MoO_3$ was present as a crystalline hydrate.

The X-ray diagrams for the investigated samples were identical, except for that with 0.6 atom fraction thallium content. Examples are shown in Fig. 1. The X-ray patterns remained unchanged after deactivation of the catalyst irrespective of the Tl content. For the sample with 0.6 Tl, new peaks appeared at $d$ = 1.72 and 2.75 Å, and peaks normally present at $d$ = 1.69, 1.75, 2.22, 2.30, and 2.64 Å disappeared. The peaks at $d$ = 6.18 and 3.10 Å sharply increased, while at $d$ = 3.52, 2.72, 2.07, and 1.91 Å the increase was not so pronounced. The intensity was strongly lowered at $d$ = 3.34 Å, while at $d$ = 6.66, 3.78, 3.26, 2.77, and 2.00 Å the decrease was more weak. Besides the increase of the signal intensity for the thallium molybdate owing to the higher Tl content, the intensities for $CoMoO_4$ and Ni $MoO_4$ and $\gamma$-$Bi_2MoO_6$ were also increased. This enhancement was compensated by a decrease of the signals for the crystal hydrates of $CoMoO_4$, $NiMoO_4$, and of the $\alpha$-

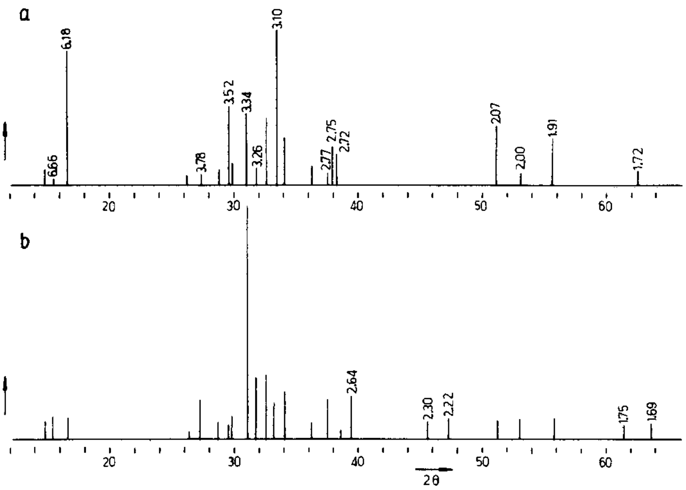

FIG. 1. X-Ray diffraction patterns of catalysts containing (a) 0.6 atom fraction Tl and (b) 0.3 atom fraction Tl.

$Bi_2Mo_3O_{12}$, respectively. It can be inferred that Tl in the higher amounts, i.e., 0.6 atom fraction, favors mainly $\gamma$-$Bi_2MoO_6$ formation. The catalyst with 0.6 Tl content also shows maximum selectivity and activity for oxidative butene dehydrogenation (*4*).

For fresh catalysts as well as those activated with steam and air, only one broad signal is obtained in the ESR spectrum and is identified as $Fe^{3+}$ with $g = 2.0$ (*5*). Six lines of $Mn^{2+}$ ions, which are used as a standard, overlap the sample's signals. The $Fe^{3+}$ ion's signal diminishes after reaction and disappears if the catalyst has not been activated before by steam and air. A new signal then appears, close to the first for $Co^{2+}$ and $Ni^{2+}$(octahedral) with identical $g$ factors equal to 2.35 (*6*), which have been concealed by the iron. Furthermore, a weak and narrow signal characteristic of $Mo^{5+}$ (*7*) appears at $g = 1.93$. In Fig. 2 are shown the ESR spectra of a catalyst with average Tl content 0.3 atom fraction before and after use. Therefore, in the absence of air the $Fe^{3+}$ ions are reduced to $Fe^{2+}$ and some of the $Mo^{6+}$ ions to $Mo^{5+}$, which affords the narrow signal overlapping with that of iron. Analogous results have also been obtained by Prasado Rao and Menon (*5*) for a catalyst with general formula $Ni_3Co_5Fe_3Bi_1P_1K_{0.1}Mo_{12}O_{52.5}$–50% $SiO_2$, which displays good activity and selectivity for propylene ammoxidation. In both cases $Fe^{3+}$ and $Mo^{6+}$ ions are reduced in the course of the reaction.

The reduction of $Fe^{3+}$ was confirmed by the ir spectra (Fig. 3) in which at 790–870 $cm^{-1}$ the signals for $Fe_2(MoO_4)_3$ at 830 $cm^{-1}$ (*5*), $Mo^{6+}$ in a tetrahedral oxygen surrounding at 800–830 $cm^{-1}$ (*2*, *8*), and $FeMoO_4$ at 790 $cm^{-1}$ (*5*) are overlapping. In the used catalyst the spectrum in this region changes and the peak maximum is shifted to 790 $cm^{-1}$, which indicates the reduction of $Fe^{3+}$

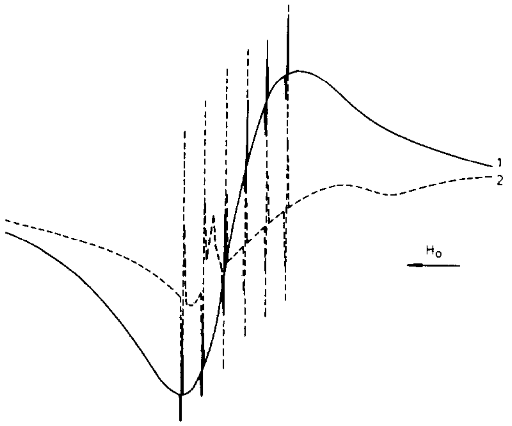

FIG. 2. ESR spectrum of a catalyst containing 0.3 atom fraction Tl before use as a catalyst (curve 1) and after use (curve 2).

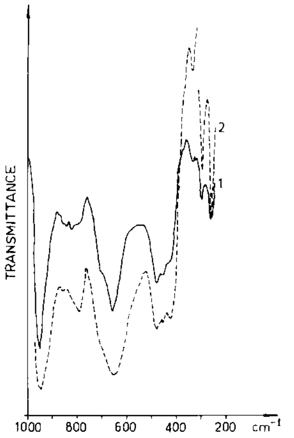

FIG. 3. Infrared spectrum of a catalyst with 0.3 atom fraction Tl before use (curve 1) and after use (curve 2).

to $Fe^{2+}$. Two peaks attributed to $Fe^{2+}$ in an octahedral oxygen surrounding (*9*) appear at 266 and 303 $cm^{-1}$. They increase in the deactivated catalyst in accordance with the results obtained.

Furthermore, the ir data show the presence of water molecules, inasmuch as peaks at 3480 and 1620 $cm^{-1}$ (*10*) are appearing. A high peak at 1130 $cm^{-1}$ attributed to the amorphous $SiO_2$ support is observed (*9*). It can be inferred on the basis of the ir spectra that the following two bismuth molybdate phases are present in the catalyst, $\alpha$-$Bi_2Mo_3O_{12}$ and $\gamma$-$Bi_2MoO_6$, as shown also by the X-ray analysis. The triplet observed at 420–490 $cm^{-1}$ is probably to be ascribed to the peaks of $\alpha$-$Bi_2Mo_3O_{12}$ at 465 and 430 $cm^{-1}$ and $\gamma$-$Bi_2MoO_6$ at 450 $cm^{-1}$ (*11*). Venyaminov (*11*) has reported some other absorption bands for both phases but in our case the peaks are overlapping there. An intense signal is obtained at 600–720 $cm^{-1}$ and attributed to the $Co^{2+}$ ion in a tetrahedral oxygen coordination (*12*). Besides cobalt, an $\alpha$-$Bi_2Mo_3O_{12}$ doublet at 665 and 715 $cm^{-1}$ and $\gamma$-$Bi_2MoO_6$ peaks on both sides of the signal at 545 and 740 $cm^{-1}$ (*11*) can appear. The peak at 340 $cm^{-1}$ is most probably to be attributed to both $Co^{2+}$ ions (*9*) and $\gamma$-$Bi_2MoO_6$ (*11*). Molybdenum in a octahedral oxygen surrounding gives a signal at 900–1000 and at 960 $cm^{-1}$ according to Batist *et al.* (*2*) and to Forzatti *et al.* (*13*), respectively, and in our spectrum there is a peak at 950 $cm^{-1}$. Therefore molybdenum is present both in tetrahedral (800–830 $cm^{-1}$) and octahedral (950 $cm^{-1}$) oxygen surrounding.

Diffuse-reflectance spectra for the 0.3 atom Tl sample before and after use as a catalyst are shown in Fig. 4. The presence of tetrahedral and octahedral molybdenum is confirmed by the unusually broad peak at 260 to 380 nm in the diffuse-reflectance spectra of all samples of the catalyst (*8, 14, 15*). The spectra show the presence of tetrahedral cobalt by a shoulder at 550–600 nm, an intense peak at 1350 nm and a weak one at 2400 nm (*16*). Some information is possibly obtained about Ni, which as $Ni^{2+}$ ion in an octahedral oxygen surrounding produces signals at 700–725 nm (*16*) and at 1350 nm, the latter overlapping with that of $Co^{2+}$. $Ni^{2+}$ ion in tetrahedral configuration also gives a signal at 1350 nm, so because of the overlapping we cannot infer whether tetrahedral nickel is present in the catalyst or not. Peaks attributed to O–H bonding in the water molecule appear at 1380, 1850, and 2100–2300 nm.

The used catalyst blackens when the reaction occurs in the absence of air and steam, probably due to reducing some of the metal oxides. As a result, the diffuse-reflectance spectra background increases and the signal intensity is lowered for all components. The decrease is very strong at 1350 nm, which indicates that $Co^{2+}$ or $Ni^{2+}$, or both of them, are reduced to the monovalent state or to metallic Co and Ni. Rushala *et al.* (*17*) have found reduction of cobalt and appearance of $Co_2MoO_4$ for a catalyst with general formula Ni(Co) $Mo_{1-3/n}P_nO_4$ on treatment with propylene at a high temperature in the absence of air.

DTA demonstrated the presence of two exothermal effects at ca. 300 and 700°C, and a small endothermal one at ca. 600°C which is probably due to a sublimation of free $MoO_3$ (*14*). The weight losses in TGA varied from 2 to 4%. The decrease in weight

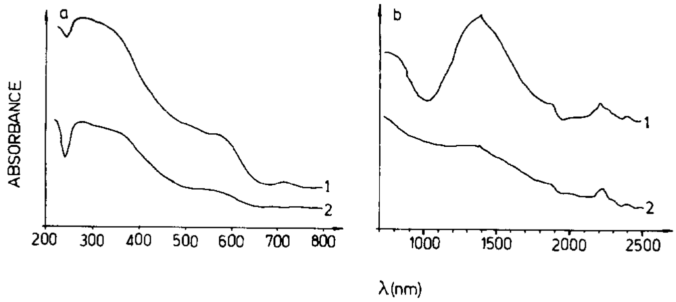

FIG. 4. Diffuse-reflectance spectra of a catalyst containing 0.3 atom fraction Tl before use (curve 1) and after use (curve 2). (a) Ultraviolet and visible region and (b) near-ir region.

occurs mainly up to 400°C, and is probably due to dehydration.

Electron micrographs revealed porous structure, which remained unchanged in the used catalyst. Some particles (5–10 $\mu$m) of the catalyst were examined for distribution of the elements included in the catalyst composition by an X-ray microanalyzer. It was found that all elements were uniformly distributed in the examined layer (up to 3 $\mu$m depth) of the catalyst particles.

It can be concluded that a mixture of Ni $MoO_4$, $CoMoO_4$, $FeMoO_4$, $Fe_2(MoO_4)_3$, $\alpha$-$Bi_2Mo_3O_{12}$, $\gamma$-$Bi_2MoO_6$, and $Tl_2Mo_3O_{10}$ is present on an amorphous $SiO_2$ support. No data referring to phosphorus have been obtained, owing to the fact that its amount in the catalyst is very low and it is concealed by the other components. Very probably phosphorus is present as phosphate ions. As compared to the other oxides in the catalyst, the molybdenum and phosphorus oxides show acidic properties and may serve as centers of negative charge, while the remaining oxides serve as positive charge centers. Since the phosphate ion possesses more strongly acidic properties than the molybdate ion, it will be neutralized before the neutralization of the molybdate ions. The electric charge balance will be given by the sum of the positive Tl, Co, Ni, Fe, and Bi charges, multiplied by the corresponding amounts, this being set against that of the negative $(PO_4)^{3-}$ and $(MoO_4)^{2-}$ ions. This balance points to a surplus of negative charge. The electric charge balance for the catalyst with maximum activity and selectivity (0.6 atom fraction Tl) is as follows:

$$\begin{array}{lcr}
\mathrm{Tl}(+1)0.6 & = & 0.6 \\
\mathrm{Co}(+2)4 & = & 8 \\
\mathrm{Ni}(+2)4.5 & = & 9 \\
\mathrm{Fe}(+3)1 & = & 3 \\
\mathrm{Bi}(+3)1 & = & 3 \\
\hline
 & & 23.6
\end{array}
\qquad
\begin{array}{lcr}
(\mathrm{PO_4})^{3-}(-3)0.08 & = & -0.24 \\
(\mathrm{MoO_4})^{2-}(-2)12 & = & -24 \\
\hline
 & & -24.24
\end{array}$$

Since no free charges can exist in the catalyst, the surplus of negative charge indicates that all oxides are present as phosphates and molybdates. A small part of molybdenum is present as $MoO_3$.

Bielanski and Haber (*18*) in a study of the catalytic properties of transition metal oxides distinguish three groups of oxide catalysts. The first group comprises oxides characterized by a high concentration of electron donor centers, which can supply electrons for oxygen adsorption. The second group of oxides has low concentration of electron donor centers. The third group is formed by mixed oxides in which oxygen is present as an oxyanion with transition metal ion in its highest oxidation state as the central atom. The oxides of the first two groups activate oxygen and adsorb it as ionic radicals $O^-$ and $O_2^-$, forming peroxy and epoxy-active complexes with the hydrocarbons and resulting in a complete oxidation. The hydrocarbon molecules adsorbed on oxides of the third group are activated by the cations acting as oxidizing agents. The lattice oxygen ion from this group has the ability to be inserted into the hydrocarbon. This is particularly favorable for selective hydrocarbon oxidation. According to the above classification our catalyst belongs to the third group of oxide catalysts in which the metallic cations are situated in a tetrahedral or octahedral oxygen surrounding. Layers of ions are formed with those of oxygen anions and metallic cations alternating.

Small amounts of Tl additives have a promoting effect in the present catalyst. When the Tl amount reaches 0.6 atom fraction, some changes appear in the catalyst structure. X-Ray analysis shows that the amount of $\gamma$-$Bi_2MoO_6$ increases, and this is accompanied by maximum activity and selectivity. There are already data in the literature about various substances promoting the formation of $\gamma$-$Bi_2MoO_6$, namely $BiPO_4$, $Fe_2(MoO_4)_3$, and $Cr_2(MoO_4)_3$ (*2*). It was found for $Fe_2O_3$, $Cr_2O_3$, CuO, $TeO_2$, and $SeO_2$ that they promote the crystallization of $\gamma$-$Bi_2MoO_6$ and $\beta$-$Bi_2Mo_2O_9$ during catalyst preparation (*19*). In addition to the effects previously found for thallium, such as lowering of the surface acidity, increase of the amount of oxygen with optimal bond energy for partial olefinic oxidation (*4*) and formation of defects in the lattice (*20*), it also probably favors the crystallization of $\gamma$-$Bi_2MoO_6$.

## CONCLUSIONS

The elements listed in the catalyst composition are present as molybdates on an amorphous $SiO_2$ support. A small amount of molybdenum exists as free $MoO_3$. Addition of 0.6 atom fraction thallium leads to structural changes in the catalyst. During the oxidative dehydrogenation of butene in the absence of air some of the $Mo^{6+}$ and $Fe^{3+}$ ions are reduced.

## ACKNOWLEDGMENTS

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