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The Selective Oxidation of 1-Butene Over a Multicomponent Molybdate Catalyst. Influences of Various Elements on Structure and Activity

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Structures, activities and selectivities were investigated of catalysts with the general formula: $Me_a^{II}Me_b^{III}Bi_cMo_dO_e$, in which Me^{II} is Ni, Co, Mg or Mn and Me^{III} is Fe, Cr, Al or Ce.

The structural and catalytic properties lead to division into two categories, one when Me^{III} is Fe, Cr or Al and the other when Me^{III} is Ce.

In the first group catalytic activity and selectivity is connected with Bi_2MoO_6 and $Bi_2Mo_3O_{12}$, present as an outer layer on a nucleus formed by $Me^{II}MoO_4$ (with β-$CoMoO_4$ structure) and $Me_2^{III}(MoO_4)_3$. The formation of Bi_2MoO_6 is promoted by Me^{III} in the sequence Fe > Cr > Al. Moreover Bi_2MoO_6 is activated by use of Fe. $Me_2^{III}(MoO_4)_3$ has been proved to be a stabilizer of the β-$CoMoO_4$ structure.

In the second group the promoter effect seems to be connected with an incorporation of Bi^{3+} in the Ce-molybdate and there is no specific preference for the β-$CoMoO_4$ structure.

INTRODUCTION

In this paper we report on the properties of a group of selective oxidation catalysts with the general formula $Ni_a \cdot Co_b \cdot Fe_c \cdot Bi_d \cdot P_e \cdot K_h \cdot Mo_f \cdot O_g$ as mentioned in a Dutch patent application 7006454 (1970). The composition of these catalysts varies over a wide range: a and b between 0 to 15, $a + b$ between 2 and 15, c from 0.5 to 7, d from 0.1 to 4, e from 0 to 4, f is 12, g from 35 to 85 and h from 0.01 to 0.5.

This group is remarkable because it contains only small amounts of a cation (Bi^{3+}) the molybdates of which are known to be active and selective for the conversion of propene to acrolein, while the majority of cations present, if applied as single molybdates are known to be inferior for this reaction both as to their activities and their selectivities.

Questions that might be asked are: (1) is Bi–molybdate still the principal catalytic compound and if so what is then the explanation of the synergetic action of the other molybdates, or conversely (2) is now the combination of the other molybdates the main catalytic agent and how does Bi–molybdate then succeed in improving its activity and selectivity?

In this investigation we approached these problems in the following manner: (a) by replacing the bivalent (Co, Ni) and trivalent (Fe) cations by related species (Co^{2+} and Ni^{2+} by Mn^{2+} and Mg^{2+}, Fe^{3+} by Cr^{3+}, Ce^{3+} and Al^{3+}) to obtain an insight into their actions; (b) by varying the amount of Fe to investigate the influence of this element on stability of catalyst structure; (c) by replacing Bi^{3+} by La^{3+}, Tl^{3+} to determine whether Bi is still the active agent.

The possible influence of silica gel, P and K was not investigated since for Bi molybdate these additives are intrinsically irrelevant and only important because of the need of a catalyst that has to stand up to technological demands (such as mechanical stability in fluid beds).

Instead of the propene–acrolein oxidation we used the related butene–butadiene oxidation as the model reaction. For the special case of Bi molybdates as catalysts this was shown to be an adequate approximation.

EXPERIMENTAL PROCEDURE

I. Preparation of Catalysts

Powdered molybdic acid was added to a stirred hot solution of $Co(NO_3)_2 \cdot 6H_2O$ in water; the atomic ratio of Co/Mo was 1. Diluted ammonia was then added until the pH was 5. A purple colored precipitate was formed. By further heating with stirring the water evaporated and a viscous slurry with pH of 3 to 4 was obtained which was subsequently dried at 110°C during 12 hr. After powdering in a mortar, precalcination at 320°C in air for 1.5 hr, the catalyst was further calcined in air at 520°C for 2 hr after which it was quickly cooled to room temperature; the color of the catalyst then was slightly purple.

This basic procedure of preparing $CoMoO_4$ was followed for preparing all the other catalysts. The elements Ni, Mg, Mn, Fe, Cr, Al, Ce, Bi, La, were incorporated during preparation by substitution of a proportional amount of cobalt nitrate by the nitrates of those elements. Used were, respectively: $Ni(NO_3)_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, $Bi(NO_3)_3 \cdot 5H_2O$, $La(NO_3)_3 \cdot 6H_2O$. Thallium was incorporated via a solution of Tl_2O_3 in concentrated nitric acid.

The preparation via evaporation of liquid was necessary since coprecipitation reactions with ammonium heptamolybdate did not lead to complete precipitation. A filtration procedure without loss of material was therefore impossible. One observation that might be important is that the Cr, Fe, Al molybdates formed in water were far more gelatinous than the other metal molybdates.

TABLE 1
LIST OF CATALYSTS

Catalyst	Surface area (m^2g^{-1})
$CoMoO_4$	6.2
$Co_{5/8}Ni_{3/8}MoO_4$	17.8
$Co_{1/2}Ni_{1/2}MoO_4$	15.4
$NiMoO_4$	28.0
$Co_{5/11}Ni_{3/11}Fe_{3/11}MoO_{4+x}$	8.7
$Co_{5/9}Ni_{3/9}Bi_{1/9}MoO_{4+x}$	4.2
$Co_{5/12}Ni_{3/12}Fe_{3/12}Bi_{1/12}MoO_{4+x}$	4.7
$Co_{5/12}Ni_{3/12}Mn_{1/12}Fe_{2/12}Bi_{1/12}MoO_{4+x}$	4.4
$Co_{5/12}Ni_{3/12}Mn_{2/12}Fe_{1/12}Bi_{1/12}MoO_{4+x}$	4.4
$Co_{5/12}Ni_{3/12}Mn_{3/12}Bi_{1/12}MoO_{4+x}$	4.3
$Co_{8/12}Fe_{3/12}Bi_{1/12}MoO_{4+x}$	4.5
$Co_{8/11}Fe_{2/11}Bi_{1/11}MoO_{4+x}$	4.2
$Ni_{8/12}Cr_{3/12}Bi_{1/12}MoO_{4+x}$	6.4
$Ni_{8/12}Fe_{3/12}Bi_{1/12}MoO_{4+x}$	5.1
$Ni_{8/12}Al_{3/12}Bi_{1/12}MoO_{4+x}$	4.4
$Ni_{8/12}Ce_{3/12}Bi_{1/12}MoO_{4+x}$	9.0
$Mn_{8/12}Cr_{3/12}Bi_{1/12}MoO_{4+x}$	3.1
$MnMoO_4$	0.7
$MgMoO_4$	4.7
$Mg_{8/11}Al_{3/11}MoO_{4+x}$	4.5
$Mg_{8/12}Al_{3/12}Bi_{1/12}MoO_{4+x}$	1.9

Catalysts of the compositions and surface areas shown in Table 1 were prepared.

II. X-Ray Measurements

Results were obtained using a Philips X-ray diffractometer with a Geiger–Müller counter and Ni-filtered Cu $K\alpha$ radiation.

Our sample of $NiMoO_4$ has the α-$CoMoO_4$ structure, as described by Smith and Ibers (*1*). Attempts to prepare $NiMoO_4$ with the β-$CoMoO_4$ structure by quenching pure $NiMoO_4$ from 520°C to room temperature were not successful. Other investigators, for instance Sleight and Chamberland (*2*), mentioned earlier that it is not possible to obtain β-$NiMoO_4$ at normal temperature and pressure.

According to the literature $CoMoO_4$, $MgMoO_4$ and $MnMoO_4$ are isomorphous: they all possess the β-$CoMoO_4$ structure (*3*, *4*), identical with α-$MnMoO_4$. The main difference between the β-$CoMoO_4$ and the α-$CoMoO_4$ structure is the oxygen coordination of Mo, which is tetrahedral in β-$CoMoO_4$ and essentially octahedral in α-$CoMoO_4$.

A combination of Co–Ni leads in our experiments to a mixture of two phases: α-$CoMoO_4$ and β-$CoMoO_4$ (see Fig. 9), while in the absence of Ni one obtains mainly β-$CoMoO_4$.

The Co–Ni–Fe combination, on the other hand, does not lead to the α-$CoMoO_4$ structure, and the β-$CoMoO_4$ structure clearly dominates. Obviously the β-form is favored by the presence of iron. Iron in this catalyst was found to be present as $Fe_2(MoO_4)_3$ in a structure similar to that reported by Plyasova and Kefeli (*5*) and by Fagherazzi and Pernicone (*6*).

The Co–Ni–Fe–Bi catalyst also shows a combination of β-$CoMoO_4$ and $Fe_2(MoO_4)_3$. The crystal structure of the Bi compound, however, is not clear, which is not surprising since only small amounts of Bi were present in the catalyst. From the presence of lines with *d*-values 3.18, 3.15 and 3.06 Å one might conclude that a bismuth molybdate, either the 2/3 or 2/1 compound, is present. However, these lines also occur for β-$CoMoO_4$ and $Fe_2(MoO_4)_3$ although with low intensities. The larger intensities observed in the Co–Ni–Fe–Bi catalyst might be an indication that bismuth molybdates are present in this system.

Catalysts, prepared with constant Co, Ni and Bi concentrations but partial replacement of Fe by Mn, show the β-$CoMoO_4$ structure together with some $Fe_2(MoO_4)_3$, the β-form apparently being stabilized by the presence of manganese. All catalysts show *d*-values of 3.18, 3.15 and 3.06 Å indicating the possible presence of bismuth molybdates. There is some indication that iron tends to promote formation of $Bi_2O_3 \cdot MoO_3$ rather than of $Bi_2O_3 \cdot 3MoO_3$, since the signal at $d = 3.15$ Å becomes relatively stronger by increasing the iron concentration (Fig. 10).

According to Plyasova and Kefeli (*5*), $Cr_2(MoO_4)_3$ and $Al_2(MoO_4)_3$ are isomorphous with $Fe_2(MoO_4)_3$. In some of our catalysts we replaced Co and Ni by Mg or Mn and Fe by Cr or Al. In all cases the bivalent metal molybdate had the β-$CoMoO_4$ structure and the trivalent metal molybdate the $Fe_2(MoO_4)_3$ structure.

Plyasova and Kefeli (*5*) suggested that $Ce_2(MoO_4)_3$ also should be isomorphous with $Fe_2(MoO_4)_3$. Our experiments, however, showed that in catalysts containing Ce instead of Fe, the $Ce_2(MoO_4)_3$ has the scheelite structure as described by Brixner, Sleight and Licis (*7*). In this structure $Ce_2(MoO_4)_3$ is isomorphous with $La_2(MoO_4)_3$.

If Ni was present in our catalysts, some $NiMoO_4$ was present as the α-$CoMoO_4$ structure, even when these catalysts contained a trivalent metal ion such as Fe, Cr or Al. This confirms the assertion of Sleight and Chamberl (*2*) that β-$NiMoO_4$ has the greatest tendency to change to the α-structure.

III. Diffuse Reflectance

To obtain more information about the surroundings of cations by oxygen, reflectance measurements were carried out (from 11,500 to 52,000 cm^{-1}) with a Unicam SP 800 spectrophotometer. The spectra are given in Fig. 1A,B,C.

a. Molybdenum (VI)

The spectra of molybdates, according to the literature, show uv peaks assigned to charge-transfer transitions $O^{2-} \rightarrow Mo^{6+}$. For MoO_4 tetrahedra two transitions are predicted. In the reflectance spectrum of, for instance, sodium molybdate Ashley and Mitchell (*8*) observed bands at 38,300 and 44,350 cm^{-1}. We found for $MgMoO_4$, in which Mo is tetrahedrally surrounded, bands at 39,000 and 45,000 cm^{-1}. Molybdates with a sixfold oxygen surrounding of Mo are reported to show an additional peak at 33,000 cm^{-1} (*8*).

For the Mg–Al–Bi–Mo catalyst we found maxima at 38,500 and 46,500 cm^{-1} (see Fig. 1A) and for this system Mo is apparently in tetrahedral coordination. The catalyst is unique because it does not show a band at 33,000 cm^{-1}, whereas catalysts containing Co, Ni or Mn always show a very broad band in this region.

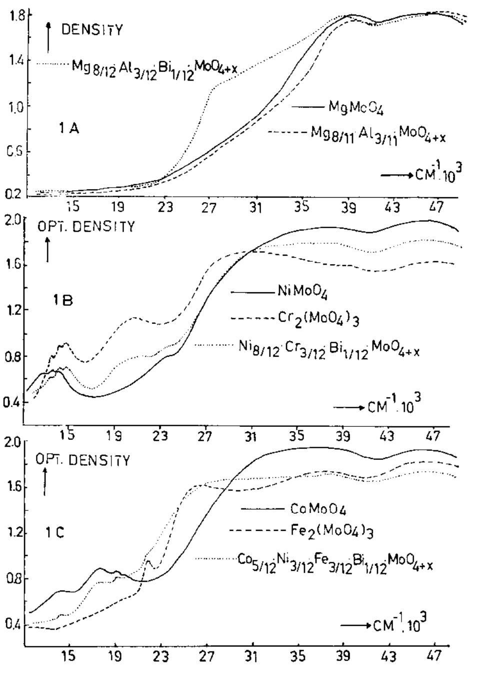

FIG. 1A, B and C. Diffuse reflectances for several catalysts.

b. *Bivalent Metals (Co, Ni, Mg, Mn)*

It was expected that the oxygen coordination of Co, Ni, Mn or Mg ions would be sixfold. Pure $CoMoO_4$ showed bands at 14,100, 17,500, 19,050 cm^{-1}, a shoulder at 19,700 cm^{-1} and a broad band starting at 25,000 cm^{-1} [charge-transfer band, see (*8*)].

The Co–Ni–Fe–Bi–Mo catalyst showed maxima at 14,100, 17,500 and 19,100 cm^{-1} and further a broad band starting at about 25,000 cm^{-1} in good agreement with the values for Co^{2+} in MgO given by Pappalardo, Wood and Linares (*9*) in which Co is octahedrally surrounded, so that we may conclude that in our catalysts Co is in an octahedral surrounding.

For samples of Ni^{2+} in MgO (octahedral), Pappalardo, Wood and Linares (*10*) gives a band at 24,270 cm^{-1} and a further five bands in the region of 13,700 to 15,400 cm^{-1}. According to him tetrahedral Ni always give a strong band at about 15,650 cm^{-1}. We found for $NiMoO_4$ a band at about 24,000 cm^{-1} and three maxima at 12,800, 13,600 and 14,200 cm^{-1} (see Fig. 1B).

For the Ni–Cr–Bi–Mo catalyst we also found a band near 24,000 cm^{-1}, but the maxima at 12,800, 13,600 and 14,200 cm^{-1} were now covered by the stronger reflections of chromium molybdate. In none of the Ni-containing catalysts did reflections occur at 15,600 cm^{-1}; we may therefore conclude that Ni is sixfold surrounded by oxygen ions.

$MnMoO_4$, in which Mn is sixfold surrounded by oxygen, shows bands at 18,000 and 23,500 cm^{-1} which are characteristic for MnO_6 octahedra. Our catalyst, containing Mn, Cr, Bi and Mo, also shows bands at about 17,500 and 23,000 cm^{-1}; these bands are weak. No other maxima were present in the spectra of this catalyst and therefore we may assume that here also manganese is surrounded by six oxygen ions.

The spectra of catalysts containing Mg give no information as to the coordination of Mg.

c. *Trivalent Metals (Fe, Cr, Al, Ce)*

Iron-containing catalysts always showed a maximum at 21,750 cm^{-1} and further a broad band starting at about 25,000 cm^{-1} (see Fig. 1C). In the spectrum of pure $Fe_2(MoO_4)_3$ we also found absorptions at 21,750 and at 26,250 cm^{-1}, these data being in good agreement with those found by other workers (*11*). We may conclude, therefore, that iron in our catalysts is octahedrally surrounded by oxygen ions, the same surrounding as in $Fe_2(MoO_4)_3$ reported by Fagherazzi and Pernicone (*6*).

In Fig. 1B the reflectance spectra of $Cr_2(MoO_4)_3$ and of a Ni–Cr–Bi–Mo catalyst are given. The absorption bands of $Cr_2(MoO_4)_3$ also appear in the Ni–Cr–Bi–Mo catalyst, maxima occurring at 13,400, 14,100 and at 14,600 cm^{-1} with a broad band at 20,500 cm^{-1}. It may be assumed that Cr in the catalyst is sixfold surrounded just as for $Cr_2(MoO_4)_3$.

The spectra of Al-containing catalysts do not show peaks that can be ascribed to this metal ion (see Fig. 1A).

The catalyst containing Ce instead of Fe, Cr or Al, did not show well defined bands.

d. Bismuth

In all the catalysts prepared, absorptions which could be ascribed to Bi were covered by stronger reflections of other elements. Probably this effect is due to the extremely small amounts of Bi used in the catalysts. However, in the Mg–Al–Bi–Mo catalyst there is a band at 27,000 cm^{-1} which has to be assigned to Bi since neither Mg nor Al show absorptions in the visible region (see Fig. 1A). It is not clear to which bismuth molybdate the band at 27,000 cm^{-1} is to be ascribed.

IV. Thermal Analysis

The apparatus applied was a Mettler Thermoanalyser T2-ES with Pt crucibles. α-Al_2O_3 heated to 1250°C was used as reference. With this instrument GTA and DTA analyses can be made simultaneously. Analysis was performed for a Co–Ni–Fe–Bi–Mo catalyst; the data are represented in Fig. 2. Only small effects were observed, in particular exothermic effects at about 690, 725 and 825°C and endothermic effects at 630, 792 and 865°C. The broad endothermic effect in the DTA curve starting from 630°C can be explained as sublimation of MoO_3. Indeed the TGA curve also showed a weight loss starting from this temperature. However, this loss is only small (of the order of 1%). The endothermic effect observed at 792°C corresponds to a melting of traces of MoO_3; its melting point is 795°C. This is in agreement with the observation that the TGA curve at this temperature becomes more flat. Melting of MoO_3 will be accompanied by a decrease of the surface of the catalyst which can lead to a decline in the rate of sublimation of MoO_3.

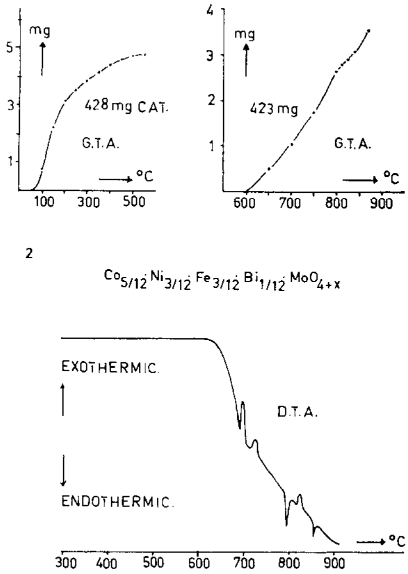

FIG. 2. (above) GTA analysis of Co–Ni–Fe–Bi molybdate catalyst; (below) DTA analysis of this catalyst.

V. Continuous Flow Catalytic Experiments

Apparatus, procedure, gas chromatographic analysis and the method of calculation have been reported earlier (*12*, *13*). In each experiment 300 mg of catalyst was used; the constant flows were 20 cm^3 min^{-1} of 1-butene and 100 cm^3 min^{-1} of artificial air.

The total amount of carbon-containing compounds is taken as 100 and gas composition is expressed in percent. In our calculations oxygen and steam values are disregarded, which is allowable as long as the oxidation is reasonably selective. Selectivity is then simply defined as:

$$[\text{diene}/(\text{diene} + 0.25CO_2)] \times 100\%.$$

Since isomerization of butenes does not play an important role with respect to the activity (isomers also are oxidized to butadiene), activity is defined as the difference in concentration of butenes before and after reaction, which implies an overall conversion in percent.

For less selective catalysts the total amount of carbon-containing products tended to decrease, in particular at higher reaction temperatures, presumably because of oxidation to liquid products such as furan and organic acids like maleic anhydride. In such cases we used a modified expression for the selectivity, i.e., as:

$$[\text{diene}/(\text{diene} + 0.25CO_2 + \text{other products})] \times 100\%.$$

in which the total concentration of other (liquid) products was determined from the decrease of the carbon balance of gaseous components.

Figure 3A and B shows the results for pure $CoMoO_4$, pure $NiMoO_4$ and for catalyst samples in which parts of Co have been exchanged by Ni. It is shown that $NiMoO_4$ is more active but less selective than $CoMoO_4$ and that the Co–Ni molybdate catalyst with the ratio Co/Ni = 5/3 possessed a reasonable selectivity and activity. Consequently in all following experiments this ratio was kept constant. During the activity test for β-$CoMoO_4$ the purple color changed via grey to olive green (the α-phase) at about 250°C. However, at 400°C the original purple color of the catalyst appeared again. The two catalysts containing Co and Ni were green before the activity tests.

Figure 4A shows the influences of iron and bismuth. The Co–Ni–Bi molybdate catalyst shows a low activity but a very high selectivity over the whole temperature range. The color of this catalyst was green and it is likely therefore that this catalyst possesses the α-$CoMoO_4$ structure. The Co–Ni–Fe molybdate catalyst, if compared with catalysts without Fe in them, showed a relatively high activity especially below 420°C; its selectivity, however, was low. Its red-brown color, presumably derived from purple β-$CoMoO_4$ mixed with yellowish green $Fe_2(MoO_4)_3$, did not change during the reaction and it seems therefore that iron stabilizes the metastable β-phase of $CoMoO_4$.

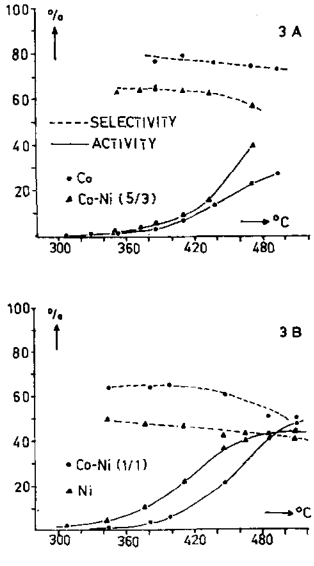

Fig. 3A and B. Activity and selectivity as a function of temperature for the following catalysts: $CoMoO_4$, $NiMoO_4$, $Co_{1/2}Ni_{1/2}MoO_4$, $Co_{5/8}Ni_{3/8}MoO_4$.

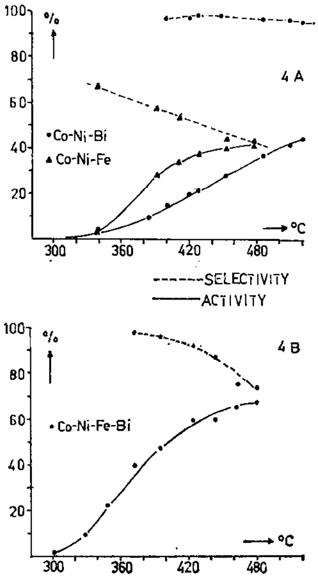

Fig. 4A and B. Activity and selectivity as a function of temperature for the following catalysts: $Co_{5/9}Ni_{3/9}Bi_{1/9}MoO_{4+x}$, $Co_{5/11}Ni_{3/11}Fe_{3/11}MoO_{4+x}$ and $Co_{5/12}Ni_{3/12}Fe_{3/12}Bi_{1/12}MoO_{4+x}$.

It is shown in Fig. 4B that activity and selectivity both increase very strongly by adding a small amount of Bi to a Co–Ni–Fe molybdate catalyst. Again the brown color of the catalyst remained unaltered during reaction (stabilization of the β-phase).

Figure 5A shows activity and selectivity of some catalysts in which iron was partly or entirely replaced by manganese. The Co–Ni–Mn–Bi molybdate catalyst with a purple color (the β-$CoMoO_4$ modification) was not very active but very selective. At about 150°C its color changed to green (α-$CoMoO_4$); we may therefore conclude that manganese only slightly stabilizes the β-modification. The selectivity of this catalyst is very similar to that of the Co–Ni–Bi

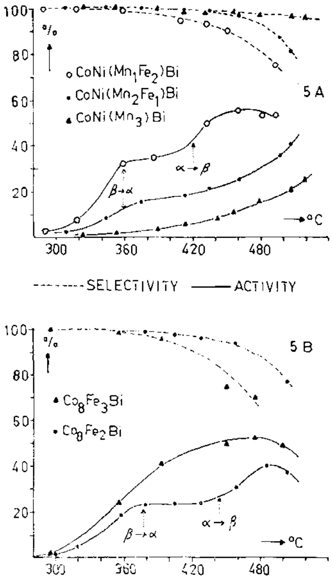

FIG. 5A and B. Activity and selectivity as a function of temperature for the following catalysts: $Co_{5/12}Ni_{3/12}Mn_{1/12}Fe_{2/12}Bi_{1/12}MoO_{4+x}$, $Co_{5/12}Ni_{3/12}Mn_{2/12}Fe_{1/12}Bi_{1/12}MoO_{4+x}$, $Co_{5/12}Ni_{3/12}Mn_{3/12}Bi_{1/12}MoO_{4+x}$, $Co_{8/12}Fe_{3/12}Bi_{1/12}MoO_{4+x}$ and $Co_{8/11}Fe_{2/11}Bi_{1/11}MoO_{4+x}$.

molybdate catalyst (Fig. 4A), its activity however being lower.

It can also be observed in Fig. 5A that the conversion of a catalyst in which 2 of the 3 parts of iron are replaced by manganese changes hardly from 360 to 420°C while in this temperature range the color of the catalyst became greenish brown, pointing to a partial transformation of the β-$CoMoO_4$ modification to the α-form. The color of the catalyst remained greenish brown at the higher reaction temperatures.

The same $\beta \rightarrow \alpha$ transformation was found during testing of a catalyst in which 1 of the 3 parts of iron was replaced by manganese. Again the flattening in the conversion was observed to start at 360°C, accompanied by a change in color of the catalyst from brown to greenish brown. However, for this sample the activity increased strongly at 420°C and the original color of the catalyst appeared again.

In Fig. 5B are represented the properties of catalysts of the following composition: $Co_{8/12}Fe_{3/12}Bi_{1/12}MoO_{4+x}$ and $Co_{8/11}Fe_{2/11}Bi_{1/11}MoO_{4+x}$ with the characteristics of the second being similar to those shown in Fig. 5A. From these experiments we may conclude that for good activity the ratio Co (or Ni)/Fe has to remain below 8/3, since if it becomes higher the structure of the catalyst will change from β-$CoMoO_4$ to α-$CoMoO_4$ with a consequent lowering of the activity.

The next activity tests are concerned with catalysts where iron is replaced by chromium or aluminum (Fig. 6A). At temperatures below 400°C the iron-containing catalyst (Ni–Fe–Bi molybdate) is the most active but not particularly selective. At higher temperatures the Cr-containing catalyst (Ni–Cr–Bi molybdate) becomes more active and remains more selective.

It is shown in Fig. 6B that the Ni–Al–Bi molybdate and the Ni–Ce–Bi molybdate catalysts are very active and selective. That not all active and selective catalysts are necessarily connected with the β-$CoMoO_4$ structure follows from the fact that our Ce-containing catalyst was about a 50–50 mixture of α- and β-$CoMoO_4$.

The results of replacements of Co and Ni

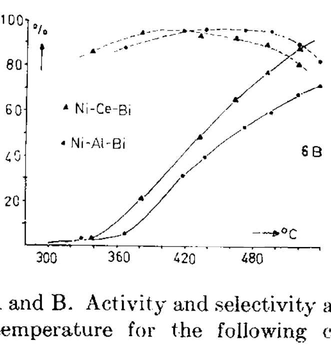

FIG. 6A and B. Activity and selectivity as a function of temperature for the following catalysts: $Ni_{8/12}Cr_{3/12}Bi_{1/12}MoO_{4+x}$, $Ni_{8/12}Fe_{3/12}Bi_{1/12}MoO_{4+x}$, $Ni_{8/12}Al_{3/12}Bi_{1/12}MoO_{4+x}$ and $Ni_{8/12}Ce_{3/12}Bi_{1/12}MoO_{4+x}$.

by Mn or Mg are shown in Fig. 7A and B. Active and selective catalysts can be obtained by such replacements, although activity seems to be a little lower with Mn- or Mg-containing catalysts.

We also tried to get some information about the function of Bi in the catalysts. Therefore we compared following catalysts: $MgMoO_4$, $Mg_{8/11}Al_{3/11}Mo_{4+x}$ and $Mg_{8/12}Al_{3/12}Bi_{1/12}Mo_{4+x}$. The results are given in Fig. 7A. It is seen that the presence of Bi leads to a strong increase in activity and selectivity.

Finally we replaced Bi by La and Tl, one element almost nonreducible and the other easy to reduce. The results are given in Fig. 8A. The La-containing catalyst is less active and selective than the corresponding Co–Ni–Fe–Bi molybdate catalyst. In the Co–Ni–Cr–Tl molybdate catalyst Tl appears to be an inhibitor for the oxidation: activity is very low, though selectivity is rather high.

For two of the best catalysts rates were plotted as a function of temperature, assuming the reaction to be first order in the butene concentration and zero order in the oxygen concentration. Log k vs $1/T$ plots show (see Fig. 8B) the now familiar picture of two intersecting straight lines with a high slope at the lower temperatures [see Batist, Prette and Schuit (*14*)]. Since no actual studies were made of the kinetics it remains hazardous to attach too much importance to this analogy but the similarity is certainly striking and it might therefore be true that butadiene is also an inhibitor for oxidation on these catalysts.

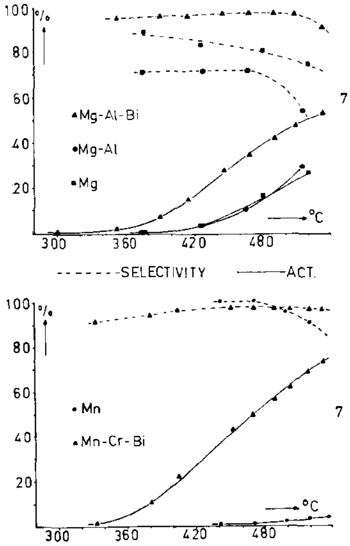

FIG. 7A and B. Activity and selectivity as function of temperature for the following catalysts: $MgMoO_4$, $Mg_{8/11}Al_{3/11}MoO_{4+x}$, $Mg_{8/12}Al_{3/12}Bi_{1/12}MoO_{4+x}$; $MnMoO_4$, $Mn_{8/12}Cr_{3/12}Bi_{1/12}MoO_{4+x}$.

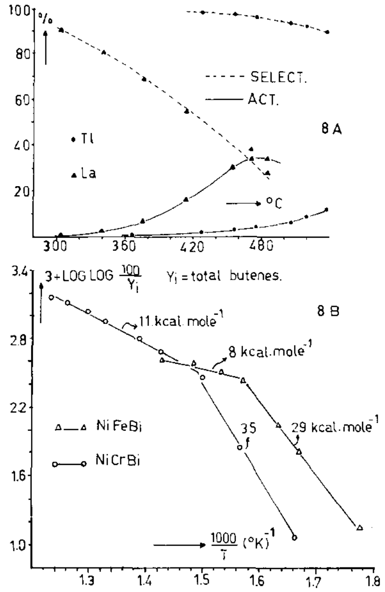

FIG. 8A. Activity and selectivity as function of temperature for $Co_{5/12}Ni_{3/12}Cr_{3/12}Tl_{1/12}MoO_{4+x}$, $Co_{5/12}Ni_{3/12}Fe_{3/12}La_{1/12}MoO_{4+x}$. (B) Arrhenius plot for continuous flow data on butene oxidation for $Ni_{8/12}Fe_{3/12}Bi_{1/12}MoO_{4+x}$ and $Ni_{8/12}Cr_{3/12}Bi_{1/12}MoO_{4+x}$.

DISCUSSION

The general composition of the catalysts studied here is:

$$Me_{8/12}{}^{II} \cdot Me_{3/12}{}^{III} \cdot Bi_{1/12} \cdot MoO_{4+x},$$

in which Me^{II} is Ni, Co, Mn, Mg and Me^{III} is Fe, Cr, Al and Ce. For reasons of stoichiometry x should be equal to 1/6.

It is convenient to separate the catalysts into two groups, one (a) with Me^{III} = Fe, Cr or Al and the other (b) with Me^{III} = Ce.

Catalysts of Group (a)

X-ray data and reflectance spectra showed that in catalysts where Me^{II} is Ni,

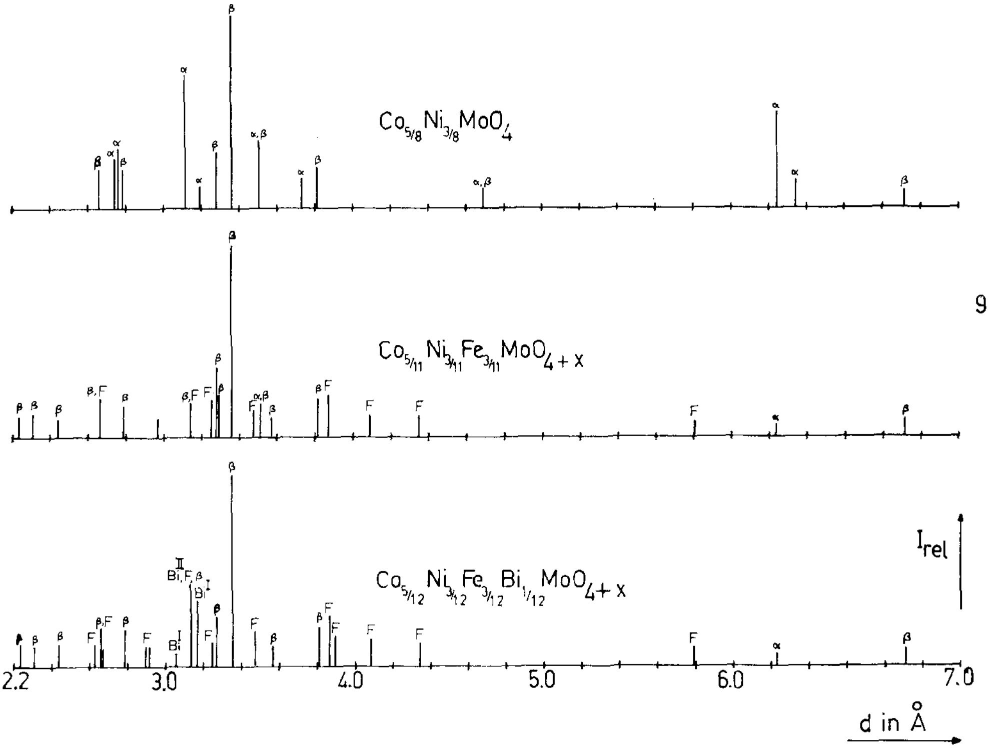

FIG. 9. X-Ray diagram with the following notation: α = α-$CoMoO_4$, β = β-$CoMoO_4$, F = $Fe_2(MoO_4)_3$, Bi^{II} = $Bi_2(MoO_4)_3$, Bi^{I} = $(BiO)_2MoO_4$.

Co, Mg or Mn and Me^{III} is Fe, Cr or Al, the $Me^{II}MoO_4$ structure is that of β-$CoMoO_4$ and the $Me_2^{III}(MoO_4)_3$ structure that of $Fe_2(MoO_4)_3$. Furthermore, Bi_2MoO_6 (2/1 phase) or $Bi_2Mo_3O_{12}$ (2/3 phase) or a combination of both is always observed. TGA and DTA analyses showed, moreover, that free MoO_3 or other free metal oxides are nearly absent.

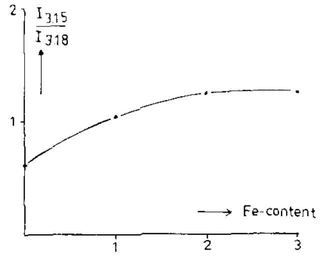

FIG. 10. Ratio of the intensities of *d*-values 3.15 and 3.18 Å as function of Fe content of the Co–Ni–Mn–Fe–Bi–Mo catalysts.

In any combination $Me^{II} + Me^{III}$ with Bi^{III} the Bi-containing catalyst is considerable more active but moreover more selective than the basis $Me^{II} + Me^{III}$. However, there is a general parallelism between activities of Bi-free and Bi-containing catalysts in that $Ni > Co > Mg > Mn$ and $Fe > Cr > Al$. On the other hand, selectivities of the Bi-containing catalysts are invariably high and do not seem to have any connection with the selectivities of the $Me^{II} + Me^{III}$ combination.

From the list of surface areas it can be concluded that if Bi is added to a system of β-$Me^{II}MoO_4$ combined with $Me_2^{III}(MoO_4)_3$ the surface strongly decreases. This suggests that Bi screens the higher surface of the earlier named combination; in other words Bi is located on the surface of the particles of the catalyst, the nucleus being formed by β-$Me^{II}MoO_4$ and $Me_2^{III}(MoO_4)_3$.

The activity per surface area and the

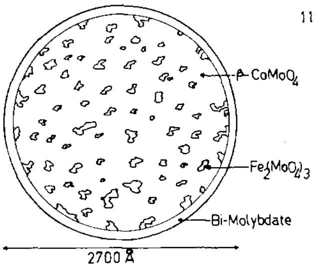

FIG. 11. Particle of active material.

selectivity of the Bi-containing catalysts are so high that nearly the whole surface of the particles has to be covered by a layer of Bi molybdate to account for these properties. If other molybdates were also present on the surface in appreciable amounts, activity and especially selectivity of the catalysts could not be so high.

It might be asked whether such low amounts of Bi molybdate are able to screen the surface of the particles of the catalyst completely and still succeed in forming layers of a thickness of dimensions to give visible reflections in X-ray measurements. From calculations on $Co_{8/12}Fe_{3/12}Bi_{1/12}MoO_{4+x}$ it appears that the particles (diameter about 2700 Å) can be covered with a layer of Bi molybdate of 100 Å (density of catalyst = 5.0 g/cm^3, density of $CoMoO_4 + Fe_2(MoO_4)_3$ = 4.3 g/cm^3, density of Bi molybdate = 6.0 g/cm^3). This should permit the observation of X-ray lines though they would be considerably broadened.

Table 2 shows that the activity per unit of surface area strongly depends on which cation (Fe^{3+}, Cr^{3+} or Al^{3+}) is used: it decreases in the sequence Fe, Cr, Al. The value of activity (expressed as a first order rate constant) per unit of surface area appears to be proportional to the ratio of intensities of the X-ray reflections of the 2/1 and 2/3 phase of Bi molybdate. This means that $Fe_2(MoO_4)_3$ is stronger than $Cr_2(MoO_4)_3$ or $Al_2(MoO_4)_3$ in promoting the forming of the 2/1 phase with regard to the 2/3 phase.

This observation explains in part the relative efficiencies of the various Me^{III} promotors: the more they tend to the formation of the 2/1 phase, the more effective they are. A possible explanation for this effect would be the relative preference of the trivalent cation for either O^{2-} or $(MoO_4)^{2-}$. If it prefers O^{2-}, $(MoO_4)^{2-}$ is donated to Bi^{III} and vice versa, i.e., the equilibrium position:

$$Me_2^{III}(MoO_4)_3^{2-} + (BiO)_2(MoO_4) \rightleftarrows Me_2^{III}O_2^{2-}(MoO_4)^{2-} + Bi_2^{3+}(MoO_4)_3^{2-}.$$

However, even taking into account this influence, it still remains unexplained why the activity per unit surface of Fe-containing catalyst appears to be higher than that of the 2/1 phase of bismuth molybdate. A

TABLE 2

CATALYTIC ACTIVITIES IN BUTENE OXIDATION[a]

Catalyst	Surface area (m^2g^{-1})	η_{380}	$k = \log 1/1 - \eta$	k (surface area)$^{-1}$	$I_{3.15} \cdot (I_{3.18})^{-1}$
(Co, Ni) Fe Bi	4.70	40.5	0.2255	0.0480	1.24
Co Fe Bi	4.50	35.0	0.1871	0.0416	1.10
Ni Fe Bi	5.04	52.0	0.3188	0.0632	1.00
Ni Cr Bi	6.35	26.0	0.1308	0.0206	0.45
Mn Cr Bi	3.06	10.5	0.0482	0.0158	0.39
Ni Al Bi	4.41	10.5	0.0482	0.0109	0.40
Mg Al Bi	1.85	5.0	0.0223	0.0120	0.39
Ni Ce Bi	8.97	21.0	0.1024	0.0114	0
Bi/Mo = 2/1[b]	4.1	27.4	0.1391	0.0339	∞
Bi/Mo = 2/3[c]	2.0	1.6	0.0070	0.0035	0

[a] η_{380} = activity at 380°C.

[b] See Ref. *(13)*.

[c] See Ref. *(15)*.

possible explanation for this phenomenon might be that Bi in catalysts with a composition of $Me_{8/12}{}^{II}Me_{3/12}{}^{III}Bi_{1/12}MoO_{4+x}$ can transfer electrons both to Mo^{6+} and to Fe^{3+} in the bulk of the catalyst, while in the Bi/Mo = 2/1 catalyst only Mo^{6+} can accept electrons from Bi. Since electron transfer from Bi to Mo or some other cation seems to be a relevant feature of the oxidation catalysis, this additional possibility of transferring electrons from the actual catalytic site might be of considerable importance. So Fe^{3+} not only promotes the formation of the 2/1 phase but moreover activates the bismuth molybdate, while Cr^{3+} and Al^{3+} do not appear able to activate the 2/1 phase, at least not at temperatures below 460°C for Cr^{3+} and 500°C for Al^{3+}.

The influence of Ni, Co, Mg or Mn on activity and selectivity of the catalysts can be explained in a similar manner since for these Me^{II} molybdates the sequence of reducibility is known to be Ni > Co > Mg > Mn.

The Co–Ni–Fe–La–Mo catalyst (surface area 7.94 m^2 g^{-1}) showed that reducibility of Bi in the other catalysts is essential. The La-containing catalyst is nonselective and is comparable with a catalyst without La.

While La^{3+} is difficult to reduce, Tl^{3+} is very easily reducible. Nevertheless, the Co–Ni–Cr–Tl–Mo catalyst (surface area 8.76 m^2 g^{-1}) is very inactive. Therefore it seems that reoxidation of this catalyst presents the main difficulty.

We still have to discuss why the β-$CoMoO_4$ structure is important in comparison with the α-$CoMoO_4$ structure and how the metastable β-$CoMoO_4$ structure (at least for Co and Ni) is stabilized by use of Fe, Cr or Al molybdate, provided that they are present in sufficient quantities. This effect is not easily explained at the present time but a possible explanation can be proposed along the following lines. In α-$CoMoO_4$, Co as well as Mo are octahedrally surrounded by oxygen ions, the Mo–O octahedra being strongly distorted. Four Mo–O distances vary from 1.72 to 1.98 Å and two Mo–O distances from 2.31 to 2.33 Å (*1*). Octahedra in α-$CoMoO_4$ are connected via edges and are forming chains parallel to the *c*-axis. Comparison with the structure of β-$CoMoO_4$ shows that the general arrangement of metal ions is the same as in the α-phase; however the positions of the oxygen ions are different. The oxygen coordination of Mo in β-$CoMoO_4$ is nearly tetrahedral while the oxygen coordination of Mo in α-$CoMoO_4$ is approximately octahedral. While in the α-$CoMoO_4$ structure the octahedra are connected via edges, in the β-structure octahedra and tetrahedra are connected via corners. The result is a less compact structure with a difference in density of about 6% (*2*).

In $Fe_2(MoO_4)_3$ the Fe–O octahedra and Mo–O tetrahedra just as in β-$CoMoO_4$ are connected via corners (*6*). The sequence of layers Co,Mo and that of Fe,Mo along the *c*-axes is closely similar. The stabilization of β-$CoMoO_4$ by $Fe_2(MoO_4)_3$ can therefore be explained by assuming that the β-$CoMoO_4$ structure is better suited than the α-$CoMoO_4$ structure to fit the $Fe_2(MoO_4)_3$ structure. This might be the reason why β-$CoMoO_4$ leads to a higher activity of the catalysts.

Catalyst of group (*b*)

Consider now the Ni–Ce–Bi–Mo catalyst, which as opposed to the other catalysts did not show a pronounced β-$CoMoO_4$ preference. It is moreover noteworthy that none of the typical Bi molybdate lines were ever found in X-ray diagrams of samples of this combination. The function of $Ce_2(MoO_4)_3$ therefore seems to be that of distributing the Bi^{3+} sites on its surface and is therefore intrinsically different from that of the other trivalent cations and presumably more similar to the situations observed by Aykan, Sleight and Rogers (*16*).

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