

The Nature of Active Components in Fe₂O₃-MoO₃ System

IV. Bi-Doped Fe(III)-Molybdate: Characterization and Activity

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An investigation on the Fe-Mo-Bi oxides system in the Fe-rich region was carried out by adding various amounts of Bi to Fe(III)-molybdate. The principal catalytic modifications which already occurred at very low Bi levels (0.5% Bi₂O₃ by wt), were: (i) strong decreasing in isomerizing power at low temperature; (ii) strong increase in the selectivity to and yield of butadiene; (iii) decrease in 1-butene conversion; (iv) strong decrease in CO formation.

The characterization of these catalysts with Mössbauer, ir, ATR, diffuse reflectance, X-rays seems to indicate that no new phase is present at these concentrations of Bi. Only at much higher levels (3.5% Bi₂O₃ by wt) where the catalytic activity is already constant, does a new phase form in increasing amounts. This new phase is Bi-molybdate 2:1 modified probably by Fe³⁺. It is proposed that the active and selective phase of these ternary systems is Fe(III)-molybdate with Bi as dopant in interstitial or substitutional sites, which might give rise to Bi(V)-Mo(VI) continuous groups.



Other particular features of these catalysts seem to be:

- i. A higher activity than that of the typical values of Bi-molybdates.
- ii. An activity constant also in very reducing conditions where Bi-molybdates become inactive.
- iii. A strong influence of oxygen partial pressure: at very low oxygen level the selectivity increases considerably.

INTRODUCTION

The reactivity in redox processes and the catalytic behavior of Fe₂(MoO₄)₃·MoO₃, alone or Te-doped, in the oxidation of CH₃OH, the epoxidation of olefins, and

the isomerization and oxidation of 1-butene have previously been investigated (1-3).

All the catalysts that were analyzed contained a large excess of MoO₃. It was advanced (3) that this excess of MoO₃ was due to the preparation method, although not necessary at least in so large a quantity, for catalytic properties.

Recently, a method of preparing Fe-

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molybdate without any MoO_3 excess by precipitation technique has been discovered (4).

Multicomponent catalysts containing Fe, Bi and Mo were considered in several investigations as reported in the Journal (5, 9) and the patent literature (10, 11). In fact, systems containing at least these three elements represent a new generation of catalysts which have successfully been used in the oxidation and ammoxidation of olefins.

However, the role of each element in such systems is not clear: some authors (5, 9) claim that a new compound containing Fe-Bi-Mo is responsible for the catalytic activity, while according to others (6, 7) the whole surface of the catalyst is covered with Bi-molybdate 2:1. In the latter case the role of Fe would be: (i) to favor the formation of Bi-molybdate 2:1 instead of the Bi-molybdate 2:3 which is rather inactive; (ii) to help Bi^{3+} in the electron transfer from Mo^{5+} .

While the above-mentioned works studied essentially modified Bi-molybdates with iron oxides the aim of the present research was to investigate the catalytic behavior of Fe-Bi-Mo oxides ternary system in the Fe-rich region; thus Fe-molybdate was modified with Bi oxides in the hope that a successful preparation of Fe-molybdate without MoO_3 excess would throw more light on the nature of the active component in these ternary systems. Indeed the addition of Bi to a matrix of Fe-molybdate containing free MoO_3 could result in the reaction of this MoO_3 excess with Bi, thus obscuring the effect of the addition of Bi to the Fe-molybdate.

Therefore, different amounts of Bi_2O_3 were added to the Fe-molybdate matrix and the catalytic activity of the resulting systems were investigated; such systems proved to be rather simple; a correlation between the presence of a possible ternary compound and the catalytic variation can therefore be attempted.

EXPERIMENTAL METHODS

All catalysts were prepared by impregnation technique starting from a matrix of Fe(III)-molybdate: this matrix was obtained by dissolving 81.6 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ in 3600 ml of water; diluted nitric acid was slowly added until pH 1.8 was reached; a solution of 120 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ in 900 ml of water was added. The vessel, containing both the yellow precipitate formed and the mother liquors, provided with a refrigerator to condense water vapor, was heated and kept boiling for 4 hr while constantly stirring; during this period the precipitate became pale green: this was filtered and washed on the filter with 500 ml of boiling water acidified to pH 2.0 with HNO_3 . It was then poured into 500 ml of nonacidified boiling water and filtered. This operation was repeated twice and finally the precipitate was dried overnight at 110°C . The matrix thus obtained was used to prepare the doped catalysts.

Then the different amounts of Bi-nitrate (RP Carlo Erba) were stirred in water (40 ml/mmmole Bi) at 80°C for 50 min. Since Bi salts hydrolyze easily, clear solutions were not obtained. Ten grams of Fe-molybdate were added. Water was then removed in about 2 hr by heating with a rotavapor at 80°C . The samples were then dried at 110°C overnight and fired at 500°C for 5 hr. The samples were labeled according to their Bi_2O_3 percentage: e.g., FM 7.3 indicated a sample containing 7.3% Bi_2O_3 by weight.

The apparatus used for the characterization of the catalysts by ir, X-ray, electronic spectra are described elsewhere (12). ATR spectra were recorded with a RIIK attachment equipped with a KRS5 crystal; surface areas were measured with a flow microcalorimeter "Microscal" (13). Raman spectra were registered with a Cary 83 spectrophotometer.

The Mössbauer absorption spectra of

TABLE 1
X-Ray Patterns of Pure and
Bi-Doped Fe-Molybdate^a

FM 0		FM 14	
<i>d</i>	%	<i>d</i>	%
6.40	6	6.36	5
5.79	13	5.78	10
4.57	8	4.55	8
4.35	18	4.35	17
4.07	24	4.078	26
3.86	100	3.87	100
3.75	11	3.76	14
3.57	17	3.56	18
3.46	29	3.46	26
3.35	9	3.35	9
3.24	21	3.24	28
3.20	10	3.20	11
3.14	6	3.15	71
2.96	20	2.96	22
2.89	8	2.89	10
2.84	10	2.84	12
		2.75	15
		2.692	3
2.63	21	2.63	28
		2.48	4
2.39	10	2.39	7
2.20	9	2.20	5
2.01	6	2.01	8
1.94	7	1.94	8
		1.92	17
1.72	17	1.72	14
		1.63	14

^a 14% Bi₂O₃ by wt.

the ⁵⁷Fe 14.4 keV γ -radiation were measured by means of a constant acceleration electromechanical driving system associated with a multichannel analyzer operating in time mode; the source was a 5 mCi ⁵⁷Co in chromium matrix kept at room temperature while the adsorbers were maintained at different temperatures in the range room temperature–500°C.

Measurements of the activity were obtained with a flow microreactor of quartz using 1 g of catalyst in each run and 110 ml/min gas mixture flow composed of 3% 1-butene 99.9% pure, 97% air. The catalyst was granulated by pressing the powder at 1300 kg/cm² for 5 min and breaking the

lamina so obtained into pieces of 1 mm diameter.

The analysis of products is described elsewhere (12).

RESULTS

The X-ray patterns of the matrix used in the impregnation (FM 0) and of a catalyst containing 14% Bi₂O₃ (FM 14) are shown in Table 1.

The pattern of FM 0 is in good agreement with the data for the Fe₂(MoO₄)₃ phase (14) that are found in the literature. No excess of MoO₃ is present in the sample; this can be checked by the absence of the peaks at *d* = 3.46 and 3.81 Å, while the most intense peak, at *d* = 3.26 Å, if present, could possibly be covered by the peak at 3.235 Å of Fe₂(MoO₄)₃.

FM 14 reveals the presence of Bi₂O₃·MoO₃ (Koechlinite) in addition to Fe₂(MoO₄)₃: this is shown by the peaks at (6, 15) *d* = 2.75; 2.69; 1.92; 1.63 Å occurring in regions free from the peaks

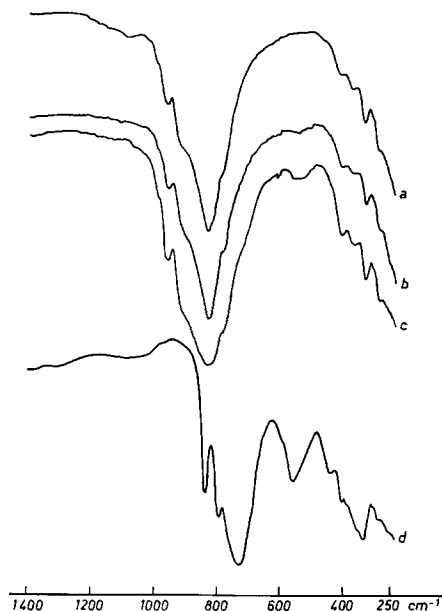


Fig. 1. Infrared spectra of the calcined samples: (a) FM 0; (b) FM 7.3; (c) FM 14; (d) Bi-molybdate 2:1.

of the Fe-molybdate matrix and by the reinforcement of the peak at $d = 3.15 \text{ \AA}$. $\text{Bi}_2\text{O}_3 \cdot 2\text{MoO}_3$ (Erman phase) and $\text{Bi}_2\text{O}_3 \cdot 3 \text{MoO}_3$ were not found in the sample (respectively, absence of peaks at $d = 2.795$; 2.699 and 1.681 \AA , and of peaks at 3.05 and 2.779 \AA , the most intense peak of both phases possibly being covered by the peak at $d = 3.15 \text{ \AA}$). We could not detect compound X found by Batist *et al.* (6) which has been recently synthesized by Sleight and Jeitschko (16) in a pure form and given the formula $\text{Bi}_3\text{FeMoO}_{12}$ and investigated by Notermann *et al.* (9); However, most of the peaks of the highest intensity of this compound are too near to those of $\text{Fe}_2(\text{MoO}_4)_3$ and $\text{Bi}_2\text{O}_3 \cdot \text{MoO}_3$ to be distinguished clearly. Peaks typical of Bi-molybdate 2:1 appear at 3.5 $\text{Bi}_2\text{O}_3\%$ only; at higher Bi concentration they increase as reported in Fig. 6.

The ir and ATR spectra are reported in Figs. 1 and 2. In addition to the bands typical of Fe-molybdate, by increasing the Bi content new bands form; these are more intense in the ATR spectra, where they are observed also at lower Bi level (FM 5). The band at 540 cm^{-1} and the broadening

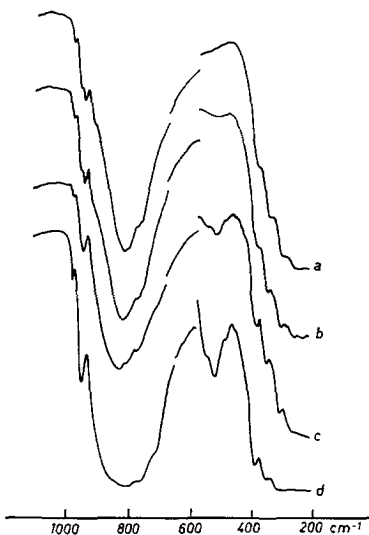


FIG. 2. ATR spectra of the calcined samples: (a) FM 0; (b) FM 5; (c) FM 7.3; (d) FM 14.

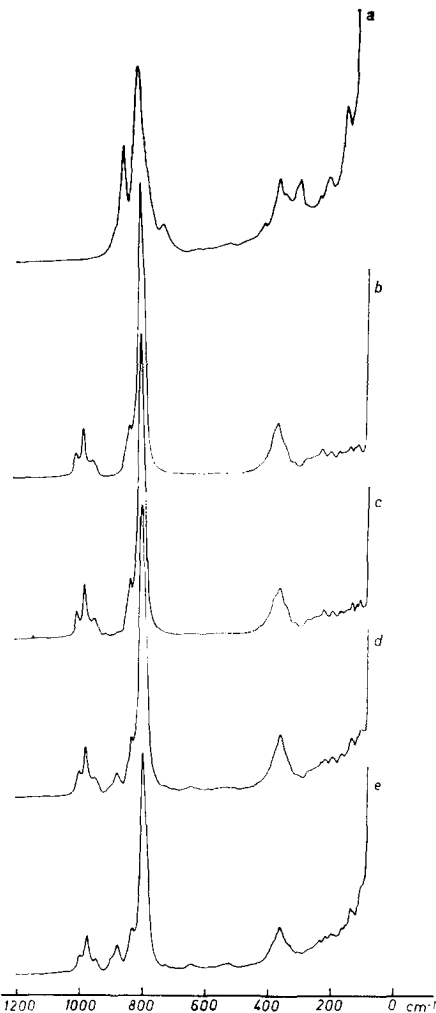


FIG. 3. Raman spectra of the calcined samples: (a) Bi-Molybdate 2:1; (b) FM 0; (c) FM 1.5; (d) FM 7.3; (e) FM 14.

of the band at 830 cm^{-1} , which is the most intense of Fe-molybdate, towards 730 cm^{-1} can easily be attributed to the presence of some Bi-molybdate 2:1, in agreement with X-ray results. It is interesting to observe that the band at 540 cm^{-1} has a complex structure in the ATR spectra showing shoulders at 555 and 500 cm^{-1} in addition to the maximum at 530 .

One possible interpretation of this datum could be the presence of some particular alteration of the bands present in Bi-molybdate 2:1. Furthermore, if one con-

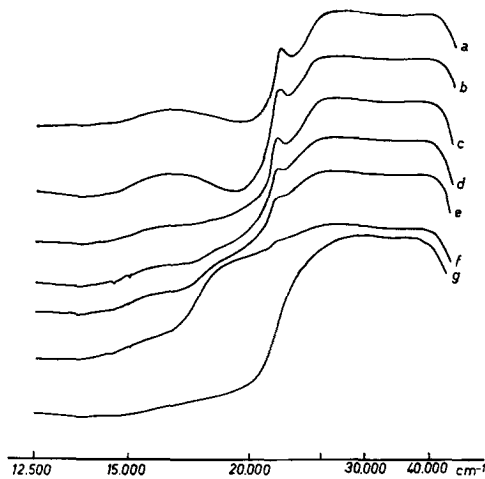


Fig. 4. Electronic spectra of the calcined samples: (a) FM 0; (b) FM 2.5; (c) FM 3.5; (d) FM 5; (e) FM 7.3; (f) FM 14; (g) Bi-molybdate 2:1.

siders that our preparation method was by impregnation technique which normally leads to higher concentrations at the surface, it is reasonable to find that the presence of this compound is more relevant in the ATR spectra.

It is also interesting to note that the band at 990 cm^{-1} typical of MoO_3 is present also at high Bi levels. Since X-ray patterns did not reveal the presence of a MoO_3 excess, only traces of MoO_3 can explain the band at 990 in the ir spectra. A possible explanation of this datum could

be a much greater reactivity of Fe-molybdate towards Bi_2O_3 than MoO_3 itself, or a difficulty for Bi_2O_3 to find a suitable pathway to reach MoO_3 located perhaps inside the Fe-molybdate structure.

In Fig. 3 Raman spectra show that for Bi_2O_3 5% by wt a new band is present which again can be attributed to Bi-molybdate 2:1 which has its second largest band at 860 cm^{-1} . However, it is found again that this band is somewhat shifted, its maximum being at 875 and it reveals a complex structure, having also a shoulder at 890 cm^{-1} .

Recalling that the band at 860 cm^{-1} is attributed to the $\text{Mo}=\text{O}$ stretching while

that at 530 cm^{-1} to $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{Mo} \quad \text{Mo} \end{array}$ bending,

we may summarize our interpretation of ATR and Raman spectra by saying that the Bi-molybdate presents some alteration as far as these bands are concerned.

In Fig. 4 the electronic spectra of samples calcined at 500°C are reported. FM 0 shows an absorption band in the visible region with maximum at about $16,400\text{ cm}^{-1}$, a characteristic absorption at $21,600\text{ cm}^{-1}$ already observed by others (6, 7) followed by a very large absorption.

Bi-Containing samples show an additional absorption in the visible region with

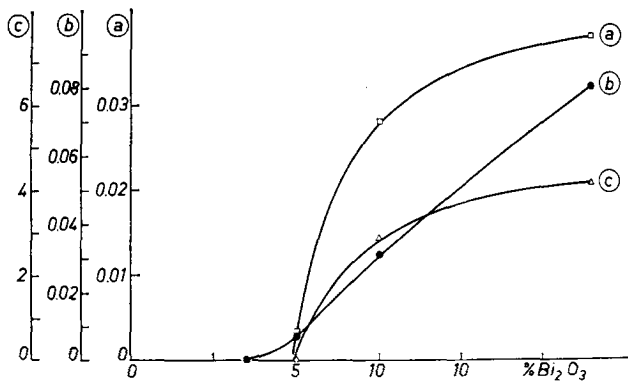


Fig. 5a. ATR modification vs Bi_2O_3 content: (a) ratio of absorbance at 530 and at 830 cm^{-1} . (b) Raman modification: ratio of the intensity of the band at 870 and the band at 785 cm^{-1} . (c) Infrared modification: ratio of absorbance at 530 and at 830 cm^{-1} .

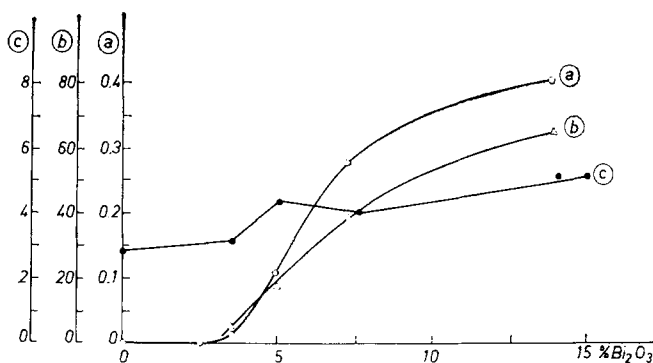


FIG. 6a. Intensity of absorption at $20,000\text{ cm}^{-1}$: $(A/R)^{1.383}$ against Bi_2O_3 content, where R = percentage reflectance $A = 100 - R$. (b) Intensity of the peak at 3.15, corrected for the value already present at 3.14 for Fe-molybdate. (c) Surface area of the catalysts (m^2/g).

a maximum at about $20,000\text{ cm}^{-1}$, which was already observed by Batist *et al.* (6). This absorption considerably broadens and increases with Bi content as shown in Fig. 6a, and was already observed in Tedoped Fe-molybdate (3) and attributed to charge transfer between Fe(III) and Te(IV). Also in this case a possible explanation is a charge transfer between Fe(III) and Bi(III). This absorption was also observed by Notermann *et al.* (9) in their ternary systems containing Fe, Mo, Bi.

In Figs. 5 and 6 an attempt is made to quantify the modifications revealed by the various techniques of investigation used vs the Bi_2O_3 content of the catalysts.

The Mössbauer absorption spectra of pure Fe-molybdate always display a single absorption line (Fig. 7a) for all the investigated temperatures. The shift is in the range typical for high spin Fe^{3+} ions and its temperature dependence has been reported already (17). The spectra of Bi-doped Fe-molybdate display a single line with a small shoulder which is relevant only at high Bi_2O_3 level (Fig. 7b). The shape of the spectra remains the same in the whole range of the investigated temperatures. The shift of the predominant line has the same values vs temperature as the ones measured for pure Fe-molybdate.

The asymmetric spectra obtained for Bi-doped samples can be interpreted as the

superposition of at least two spectra: (i) a single line due to Fe^{3+} ions of pure Fe-molybdate; (ii) an unresolved spectrum probably due to Fe^{3+} ions located in distorted sublattices. Since the contribution of the single line to the spectra of Bi-containing samples is predominant, the main portion of the doped samples is still the Fe-molybdate matrix. This is in agreement with the results obtained by the other techniques.

In Fig. 8 the results of 1-butene oxidation runs obtained with a continuous integral flow reactor are plotted vs working

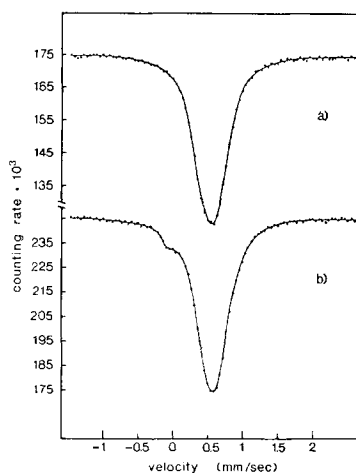


FIG. 7. Room temperature Mössbauer spectra of pure (a) and Bi-doped Fe-molybdate (14% Bi_2O_3 by wt) (b).

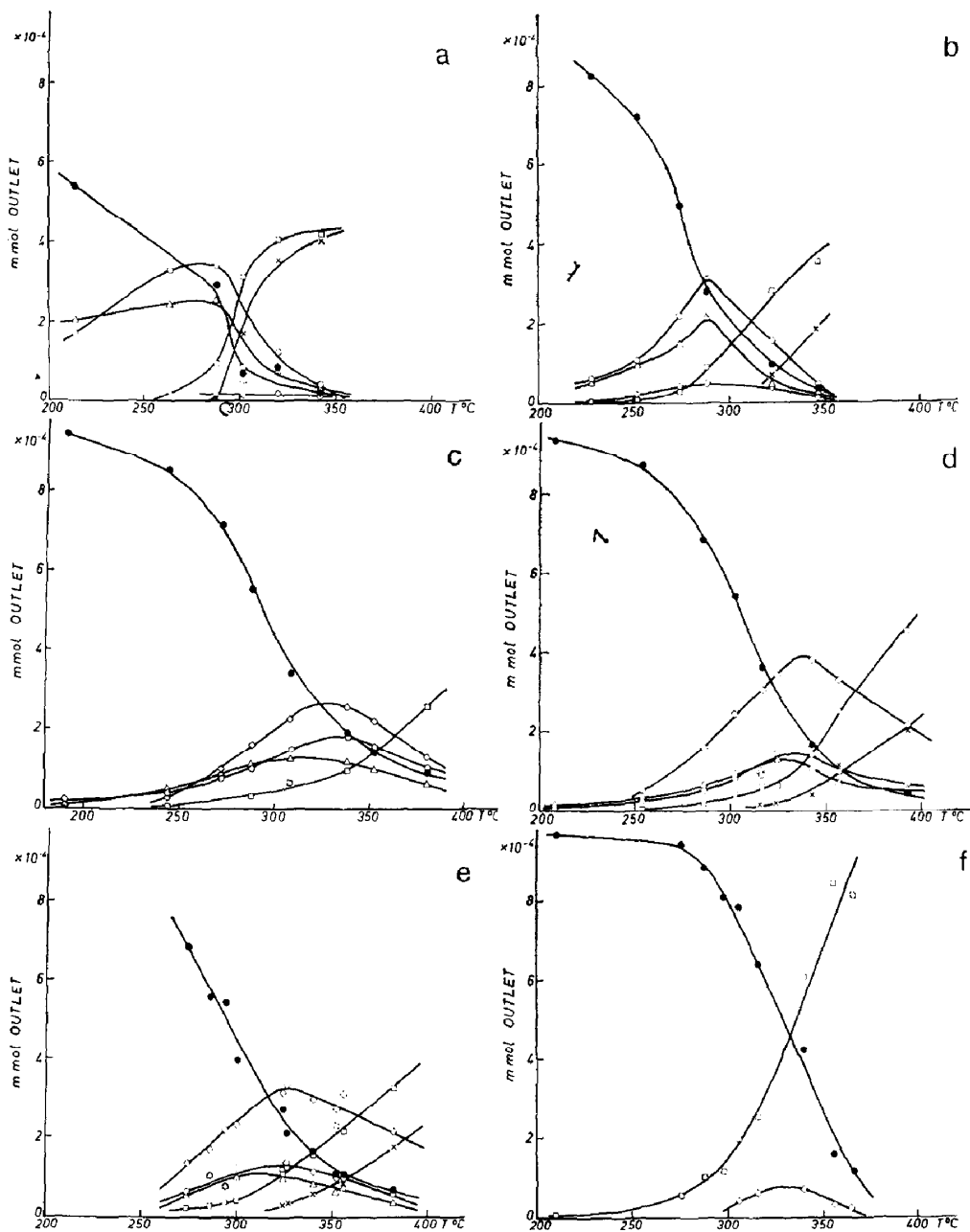


FIG. 8. Millimoles in the exit gas against working temperature. Basis: 10×10^{-4} millimoles of inlet 1-butene. Symbols: (●) 1-butene; (○) *trans*-2 butene; (△) *cis*-2 butene; (◇) butadiene; (×) CO; (□) CO₂; (a) FM 0; (b) FM 0.07; (c) FM 0.5; (d) FM 5; (e) FM 14; (f) Fe₂O₃.

temperature. For the sake of brevity the results of only 4 catalysts with different Bi content are displayed together with Fe₂O₃ and undoped Fe-molybdate.

The most important data obtained from all the catalysts tested are summarized in Fig. 9, in which the conversion, the selectivity and the isomerization power are

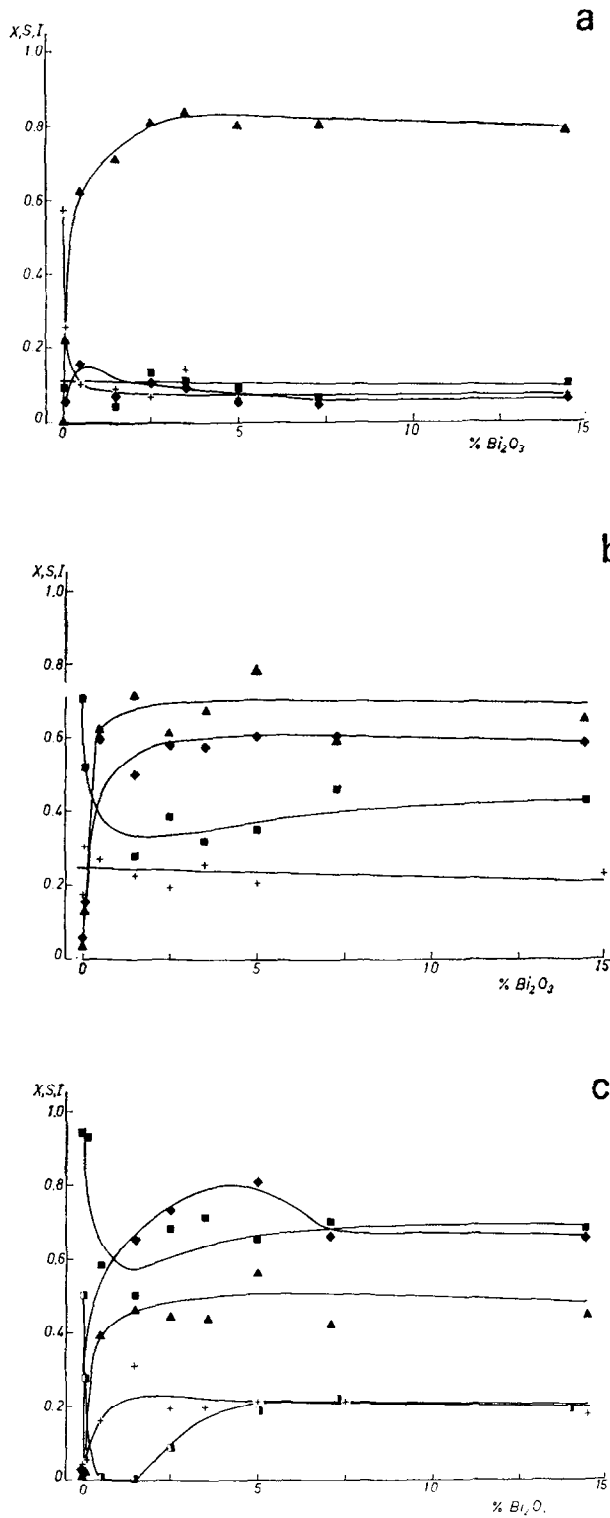


FIG. 9. Values against Bi_2O_3 content in catalysts at working temperature: (a) 260°C; (b) 310°C; (c) 350°C of: (■) conversion = (1-butene inlet - 1- and 2-butenes outlet)/1-butene inlet \times 100; (▲) selectivity = butadiene; butadiene + $(\text{C}_4\text{H}_6/4) + (\text{CO}/4)$; (+) isomerization power = (cis- + trans-2-butene outlet)/1-butene inlet; (◆) butadiene yield data normalized to the contact time of FM 0; (◼) CO/CO₂ (only at 350°C).

TABLE 2

Kinetic Parameters for Fe-Molybdates with Different Level of Bi in the Oxidation of 1- and 2-Butenes

	k_{app} (sec ⁻¹) ^a		E_{app} ^b	T (°C) 20% ^c
	At 265°C	At 320°C		
FM 0	0.053	0.633	23	288
FM 0.07	0.063	0.520	20	286
FM 0.5	0.060	0.290	13.5	281
FM 5	0.053	0.257	12.8	286
FM 14	0.086	0.350	12.3	276

^a Apparent rate constant.

^b Apparent energy of activation.

^c Temperature of 20% conversion.

plotted vs Bi₂O₃ content at 3 temperatures (260, 310, and 350°C). In the same figure the butadiene yield is given; the experimental values were corrected to take into consideration the difference in surface area of the samples which results in different contact times. The assumption made was the reaction to be first order with butene and zero order with oxygen. The CO/CO₂ experimental ratio is also given, but only for 350°C.

In order to throw some light on these catalytic data, in Table 2 are plotted the values of the apparent energy of activation E_{app} , the apparent rate constants, k_{app} , and the temperature at which 20% conversion was obtained, (T 20%), in the oxidation of 1- and 2-butenes.

In the elaboration of the experimental data it was taken into account that the reactor used was of the integral type and that different surface area resulted in different contact time; calculations were made assuming the reaction to be first order with the sum of 1- and 2-butenes partial pressure, and zero order with oxygen partial pressure at $T > 340^\circ\text{C}$, as we found on reaction runs not reported here (18). T 20% on the contrary are nonelaborated experimental values.

Figure 10 shows the change in the outlet

composition of 1-butene oxidation runs at 340°C obtained by varying the O₂ content in the inlet mixture and keeping constant the contact time with the necessary N₂ dilution.

DISCUSSION

Bi as Catalytic Promotor

As it can be observed in Fig. 9, the principal catalytic modifications have already occurred at 0.5% Bi₂O₃ by wt, i.e.:

- i. Strong decrease of isomerizing power at low temperature.
- ii. Strong increase in the selectivity to and yield of butadiene.
- iii. decrease in 1-butene conversion.
- iv. Strong decrease in CO formation also at temperatures at which CO₂ is formed.

At higher Bi levels up to 14% by wt no other great variation occurs apart from the formation of some CO at $T > 340^\circ\text{C}$.

From Table 2 one can deduce that Bi-doped Fe-molybdate has a much greater k_{app} while E_{app} and T 20% are much lower than the values normally found in the literature (6). For this reason it is possible to state that the catalytic systems here reported differ from Bi-molybdates and from the other Bi-Mo-Fe ternary systems.

Furthermore, the maximum of selectivity present at 350°C is characteristic of these systems while the others are selective also

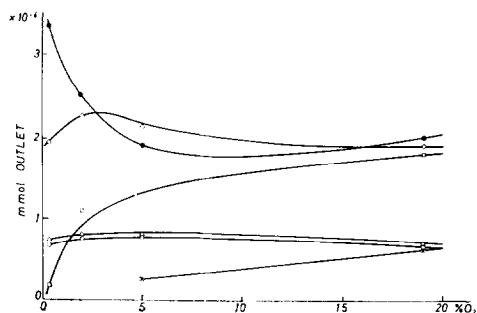


FIG. 10. Millimoles in the exit gas against %O₂ at the inlet. Catalyst, FM 14; $T = 338^\circ\text{C}$. Symbols as in Fig. 8.

at higher temperature. In order to explain the nature of this maximum it is interesting to consider the oxidation runs at low O_2 partial pressures (Fig. 9); indeed the catalysts of the present paper become selective at low O_2 levels; therefore, at temperature higher than 340°C these systems become very sensitive to the O_2 partial pressure: by decreasing the O_2 level, the selectivity increases. This effect was not found for Bi-molybdates but was observed for other systems (19) in the oxidation of 1-butene.

Chemical Modifications of the Catalysts

All the spectroscopic measurements (ir, ATR, Raman, diffuse reflectance, X-ray, Mössbauer) lead to the following conclusion (Figs. 5, 6, 7).

i. For Bi_2O_3 3.5%, in addition to the original Fe-molybdate, only one other compound, namely Bi-molybdate 2:1, is formed. Fe-Molybdate is still the main compound present.

ii. A comparison of the ir, the electronic and the Mössbauer data with those reported by Noterman *et al.* (9) leads to the conclusion that the samples are not the same.

iii. The Bi-doped samples are not simply a mixture of Bi-molybdate 2:1 and Fe-molybdate phases, since the Mössbauer spectra of pure and doped Fe-molybdate are different. The additional shoulder detected for high Bi-containing samples can be explained by hypothesizing that Bi ions set themselves in lattice sites of Fe-

molybdate structure distorting part of the iron octahedral sites or that Fe^{3+} ions migrate into empty sublattices of the Bi-molybdate structure. Accordingly, the additional absorption at $20,000\text{ cm}^{-1}$ observed in the diffuse reflectance spectra is probably due to a charge transfer between Fe and Bi ions as also advanced by Noterman *et al.* (9) for their ternary systems and by Pasquon *et al.* (3) for the Fe, Te, Mo systems. A closeness of Fe and Bi inside the same lattice must be advanced to interpret the modification of the Mössbauer and diffuse reflectance spectra. The fact that these modifications were detected only in the region where Bi-molybdate 2:1 forms suggests that Fe^{3+} ions migrate into sublattices of the Bi-molybdate 2:1. This interpretation is also in agreement with the splittings of the bands typical of Bi-molybdate 2:1 observed in the ir, ATR and Raman spectra, which also indicate an alteration of the bands of the Bi-molybdate 2:1 phase.

Nature of the Active Component

A problem still to be dealt with is what happens for concentrations below 3.5% Bi_2O_3 by wt. The catalytic measurements show that strong modifications of the catalytic properties already occur at very low concentration of bismuth. The question therefore rises as to what phase the high selectivity observed when bismuth is added to Fe(III)-molybdate should be attributed. It is possible that some Bi-molybdate 2:1

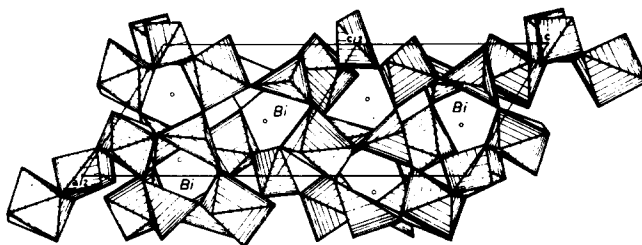
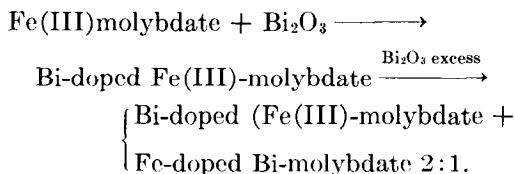


FIG. 11. $\text{Fe}_2(\text{MoO}_4)_3$ structure [from Ref. (14)] in which are shown the holes where bismuth can be accommodated.

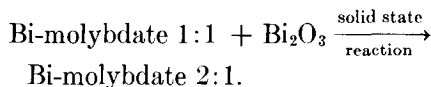
could be present at the surface of Fe(III)-molybdate also at concentration lower than 3.5% and not detected by the spectroscopic techniques used. However, we do not attribute the increase of the selectivity to the formation of this phase even if present as a surface layer for the following reasons: (i) the amount of bismuth necessary for the modification of the catalytic properties is very limited, about 0.5% Bi₂O₃ by wt, even considering that the impregnation technique might localize it first at the surface: 0.5% Bi₂O₃ by wt corresponds to about 1 Bi atom/25 Å²; (ii) no other modification of the catalytic properties was observed in the region where Bi-molybdate 2:1 was detected and found in increasing amounts in all the techniques used; (iii) the activity of the Bi-doped samples is lower than that of pure Fe(III)-molybdate, thus suggesting a modification of this phase; (iv) the strong influence of the oxygen partial pressure onto the selectivity at high temperature: this influence was not observed for Bi-molybdates. On the contrary other authors have already observed for the Fe-Mo-Bi system (5) that the activity remains constant also in very reducing conditions where Bi-molybdates become inactive. For all these reasons the active component seems to be Fe(III)-molybdate doped by bismuth.

The surface of the catalyst is probably the first to be involved in the doping process; moreover the Bi-doped Fe(III)-molybdate could be the intermediate compound that after the interaction with a further amount of bismuth segregates the Bi-molybdate 2:1 with a selective process, according to the scheme:



The fact that only one particular Bi-molybdate phase among all the possible

ones form with a remarkable selectivity is probably due to a difficult abstraction from the Fe(III)-molybdate of the Mo necessary for the formation of the new Bi-molybdate 2:1 phase. In this process the phase with the highest Bi/Mo ratio is favored. A similar selective reaction which gives rise to only a new phase is already known:



As far as the sites where Bi could be located inside Fe(III)-molybdate are concerned two hypotheses can be advanced: the first one is based on the fact that some Mo is abstracted from the Fe(III)-molybdate to form the Bi-molybdate 2:1 phase: as we had no spectroscopic nor catalytic evidence of the formation of free Fe₂O₃ (in such a case CO would not be present among the products), it is likely that some Bi ions substitute Mo in part inside the Fe(III)-molybdate structure. In this case the oxidation state of Bi would probably be the highest, i.e., Bi(V). The second possibility is that Bi ions set themselves in interstitial lattice sites as the Fe(III) structure is a very open one (see Fig. 11). Also in this case the oxidation state V of Bi is more likely due to the smaller dimension of BiV. It is known that a typical feature of Bi(V) is to give rise to Bi=O double bond with oxygen. The addition of Bi to Fe(III)-molybdate could therefore have as a result the formation of contiguous groups of the type Bi(V)—Mo(VI) in analogy to what



was already proposed for the U-Sb (20) Fe-Sb (21) and Sn-Sb (22) systems.

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