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The Catalytic Oxidation of 1-Butene Over Bismuth Molybdates

Promoters for the $Bi_2O_3 \cdot 3MoO_3$ Catalyst

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The effect of the promoters $BiPO_4$, Fe_2O_3, and Cr_2O_3 on the catalytic activity of the moderately active $Bi_2O_3 \cdot 3MoO_3$ catalyst (2/3) were investigated for the oxidation of butene to butadiene. All compounds if present in quantities equivalent to 10% (mole ratio's) show a pronounced promoting effect. For two of the three promoters, $BiPO_4$ and Fe_2O_3, it could be shown that for these concentrations the promoter action is caused by the formation of the far more active $Bi_2O_3 \cdot MoO_3$ (Koechlinite) phase (2/1). This conclusion is consistent with the observations that the 2/1 lines appear in the X-ray diagrams. The kinetics of the reaction shift to those earlier observed for the 2/1 phase and finally that the adsorptive properties for butene and butadiene become more similar to those earlier reported for 2/1 than for 2/3. The catalytic properties of the system $Bi_2O_3 \cdot 3MoO_3 + Fe_2O_3 \cdot 3MoO_3$ were studied in the entire range from Bi to Fe. It was found that a new compound (X) is formed possessing an X-ray diagram not earlier found by us but occasionally reported on technical Bi–Mo catalysts by other authors. The compound X exists along the entire range from Bi to Fe = 8/2 to 1/9. It possesses a fairly strong activity for the butene–butadiene conversion and is also a selective catalyst.

INTRODUCTION

In an earlier report (*1*) concerning the activity of various Bi–Mo compounds vs the catalytic oxidation of butene we concluded that the unsupported, white $Bi_2O_3 \cdot 3MoO_3$ (2/3) catalyst was only moderately active for this reaction while the yellow $Bi_2O_3 \cdot MoO_3$ (Koechlinite 2/1) modification showed a strong activity. The measurements were performed on samples, prepared by an unconventional and novel technique, not by fast coprecipitation but by prolonged heating of hydrated oxides. However, successful technical catalysts (*2*) for the ammonoxidation of propylene, supposedly a similar reaction as the butene conversion, have a composition that is more near to the 2/3 phase; they contain a certain amount of phosphorus, and are supported on SiO_2. Aykan (*3*), who followed the SOHIO procedure of preparation (*2*), reported the presence of traces of 2/1 and of $BiPO_4$ in this catalyst after the final calcination, and $BiPO_4$ has been found by Voge *et al.* (*4*) to possess a moderate activity for the ammonoxidation. The combination of these experimental findings raises the point of how to explain the supposedly promoting actions of compounds other than the Bi–Mo phases. This represents an interesting problem in other aspects. It is known for instance that $Fe_2O_3 \cdot 3MoO_3$ is an outstanding catalyst for the oxidation of CH_3OH to HCHO but is only weakly active for the propene and butene oxidation; one would like to know whether this is due to the replacement of Bi^{3+} by Fe^{3+} or whether the simultaneous change in the structure of the inorganic system is the main cause of the difference. If so, it might perhaps be possible to build in a limited amount of Fe^{3+} ions in the Bi–

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molybdates and study the changes connected herewith. It would also be interesting to know how a cation such as Cr^{3+} which forms a molybdate, similar in structure to the Fe^{3+} compound, but which is moreover more difficult to reduce than Fe^{3+}, would affect the butene conversion. Hence our choice of the three promoters to be investigated is, $BiPO_4$ $Fe_2O_3 \cdot 3MoO_3$ and $Cr_2O_3 \cdot 3MoO_3$. In view of the composition of the technical catalyst and because it would be easier to demonstrate promotional activities for a moderately active compound such as $Bi_2O_3 \cdot 3MoO_3$ than for its more active 2/1 counterpart, the 2/3 compound was chosen as the catalyst to be promoted. In an earlier investigation, published by Matsuura and Schuit, the adsorptive properties for butene, butadiene, O_2 and H_2O were determined on the various Bi–Mo compounds. It was shown that a catalyst active for the oxidation of butene has to possess two separate adsorptive centers, one that is connected with the adsorption of butene and another that seems to furnish the catalyst O^{2-} ion concerned with the oxidation. The substantial decrease in the activity of the Bi–molybdates in passing from the 2/1 to the 2/3 phase was found to be reflected in a strong decrease in the number of centers responsible for the adsorption of butene and a change in the number and properties of the second center. Evidently, any investigation into the effects of promotion should be completed by a parallel study on the changes in adsorption. Of course, in view of the possibility for the formation of new compounds in the ternary or quaternary systems the investigation should include studies of the X-ray diagrams, infrared adsorption and visible and ultraviolet reflection spectra. The results of this investigation will be found in the following pages.

EXPERIMENTAL PROCEDURE

Catalyst Preparations, Surface Area, and Thermal Analysis

(A) $Bi_2O_3 \cdot 3MoO_3$–$BiPO_4$ catalyst with a Mo–P ratio of 12. To a solution containing 7.27 g $Bi(NO_3)_3 \cdot 5H_2O$ a solution of 1.98 g $(NH_4)_2HPO_4$ was added and the precipitated $BiPO_4$ was filtered and washed. Then freshly precipitated and washed $Bi(OH)_3$ (from a solution containing 48.5 g $Bi(NO_3)_3 \cdot 5H_2O$) was mixed with 24 g H_2MoO_4 and the $BiPO_4$. The white coloured mass was diluted with water and boiled and stirred for 20 hr after which a slightly yellow coloured mass was obtained. After filtration and drying at 110°C the powder was calcined at 500°C for 2 hr. This catalyst was slightly yellow in contrast with $Bi_2O_3 \cdot 3MoO_3$ which is white.

(B) $Bi_9FeO_{15} \cdot 15MoO_3$ catalyst. A solution containing 87.3 g $Bi(NO_3)_3 \cdot 5H_2O$ and 8.08 g $Fe(NO_3)_3 \cdot 9H_2O$ was treated with ammonia to obtain a coprecipitate of $Bi(OH)_3$ and $Fe(OH)_3$. The brown coloured mass was filtered and washed free from ammonia and salts, after which it was mixed with 47.5 g H_2MoO_4. The total mass, diluted with water, was stirred and boiled for 12 hr until a yellow mass was obtained and a colourless solution. After evaporation of water and drying at 110°C the slightly beige yellow powder was calcined at 520°C for 2 hr. A deep yellow catalyst was obtained.

Notes. A similar method of preparation was used for $Bi_2O_3 \cdot 3MoO_3$–$Fe_2O_3 \cdot 3MoO_3$ samples with increasing Fe content. Yellow catalysts were obtained up to a Fe–Bi ratio of 5/5. Samples with more Fe in them appear brownish. Pure $Fe_2O_3 \cdot 3MoO_3$ was prepared via precipitation from a $Fe(NO_3)_3 \cdot 9H_2O$ solution with an ammonium molybdate solution. The yellow green gel obtained was dried and calcined at 500°C for 2 hr. The product was green.

Coprecipitation of $Fe(OH)_3$ and $Bi(OH)_3$ is found to be essential in the preparation of promoted Bi–Mo = 2/3 catalyst. Samples prepared with $Fe_2O_3 \cdot 3MoO_3$ instead of $Fe(OH)_3$ as the raw material proved to be inactive. The pH of the solution of the boiled masses is very important. At too low pH values a green coloured solution appears and after evaporation of water the catalyst is covered by precipitated iron molybdate. Adding ammonia to reduce the acidity did not produce an active catalyst because as well as precipitating free

$Fe(OH)_3$ soluble $(NH_4)_2MoO_4$ was also formed which finally covered the catalyst as MoO_3 making it less active. One has to adjust the pH 5–7. The Cr^{3+} promoted $Bi_2O_3 \cdot 3MoO_3$ catalyst was prepared according to the same procedure as described for the $Bi_9FeO_{15} \cdot 15MoO_3$ catalyst. $Bi(OH)_3$, $Cr(OH)_3$, and H_2MoO_4 were used as the raw materials.

Surface Area

An areameter was used and the data are collected in Table 1.

TABLE 1
SURFACE AREAS OF PURE $Bi_2O_3 \cdot 3MoO_3$ AND OF PROMOTED CATALYSTS

Catalyst	S (m^2g^{-1})	Catalyst Fe–Bi–Mo	S (m^2g^{-1})
$Bi_2O_3 \cdot 3MoO_3$	4.6	2/8/15	3.7
$Bi_9FeO_{15} \cdot 15MoO_3$	4.7	3/7/15	3.4
$Bi_8(MoO_4)_{12}$–$BiPO_4$	3.5	4/6/15	4.4
$Bi_9CrO_{15} \cdot 15MoO_3$	3.6	5/5/15	1.9
$Fe_2O_3 \cdot 3MoO_3$	6.2	6/4/15	3.5
		7/3/15	4.9
		8/2/15	4.5
		9/1/15	2.0

Thermal Analysis of the Dried Fe–Bi–Mo = 5–5–15 Sample

The data are presented in Fig. 1. (i) Differential thermal analysis. The apparatus used was the license CNSR model M-1 with Pt crucibles with α Al_2O_3 heated to 1250°C as reference. A small exothermic effect was observed at 500°C, probably residual reaction of traces of iron oxide with traces of molybdenum oxide. At 700°C the sample transformed into a liquid while simultaneously the colour changed to black. At 820°C MoO_3 started to sublime. (ii) Thermal Gravimetric Analysis with a Stanton balance. Similar to pure Fe molybdate all hydrate water was evaporated at 400°C, which is about 100°C lower than for Bi molybdate.

X-Ray Analysis

The X-ray studies were limited to the systems $Bi_2O_3 \cdot 3MoO_3 + Fe_2O_3 \cdot 3MoO_3$ and $Bi_2O_3 \cdot 3MoO_3 + BiPO_4$.

$Bi_2O_3 \cdot 3MoO_3 + BiPO_4$. The X-ray diagrams were obtained with a Philips X-ray diffractometer with Geiger–Müller counter and Ni-filtered CuK α radiation. Diagrams for Bi–Mo = 2/3, $BiPO_4$ and the promoted catalyst are shown in Fig. 2. The promoted

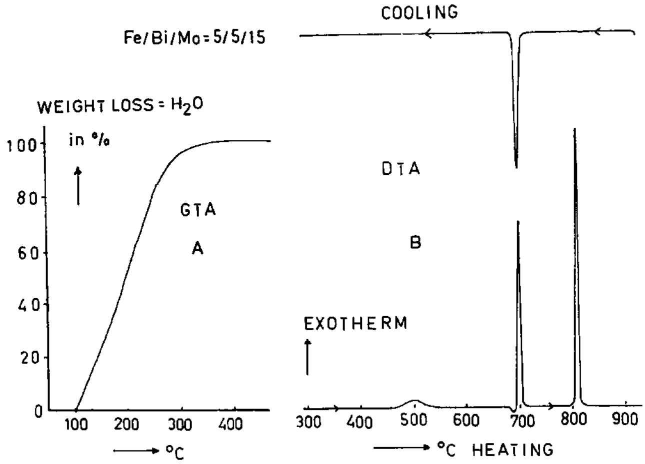

FIG. 1. (A) Loss of water during calcination of a dried Fe–Bi–Mo = 5/5/15 sample measured with a thermogravimetric balance, linear speed 6°C min^{-1}. (B) Differential thermal analysis on the dried Fe–Bi–Mo = 5/5/15 sample.

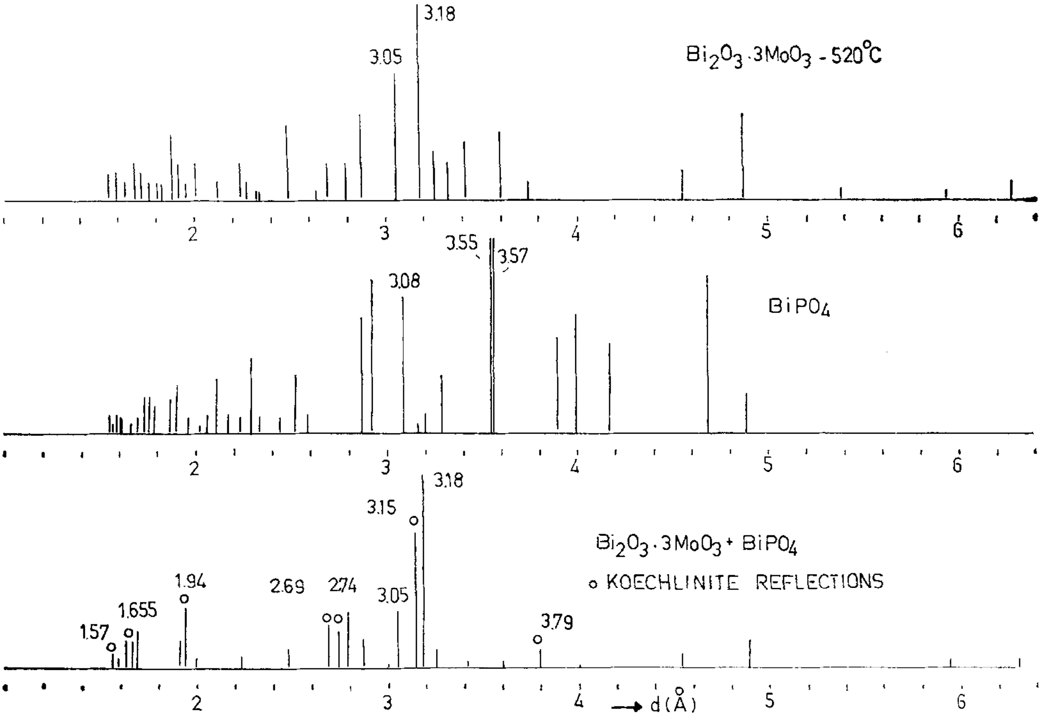

FIG. 2. Survey of X-ray diffraction patterns of a P-promoted catalyst.

catalyst showed no $BiPO_4$ lines while the intensity of the 2/3 reflections proved markedly decreased in comparison to the unpromoted sample. A number of new reflections are in the promoted sample, they are indicated by o and can be identified as belonging to the $Bi_2O_3 \cdot MoO_3$ (Koechlinite) phase (lines observed $d = 3.15$, 2.74, 2.69, 2.48, 1.920, 1.615, 1.630, and 1.575 Å).

Bi_2O_3–$3MoO_3$ + $Fe_2O_3 \cdot 3MoO_3$. A num-

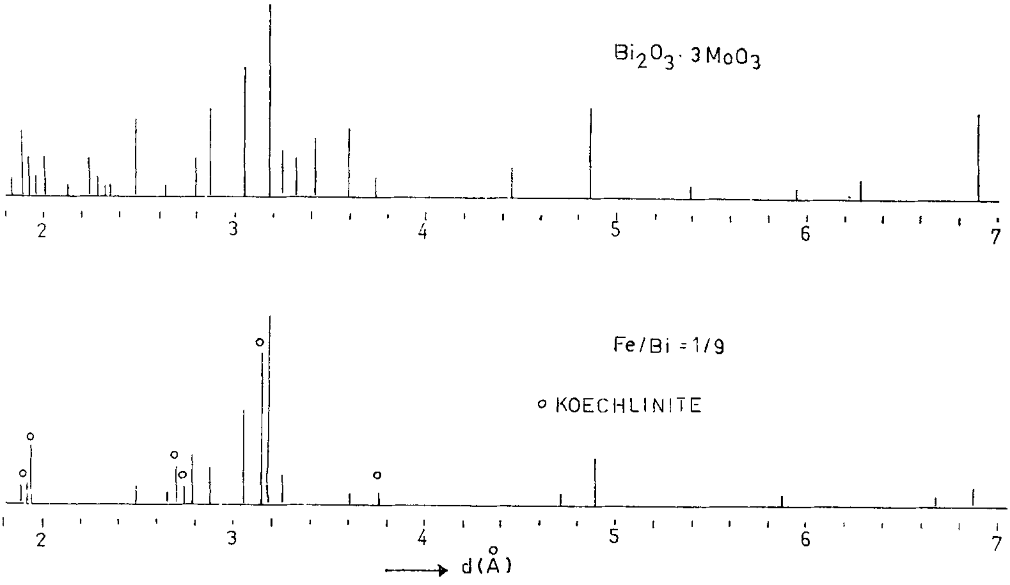

FIG. 3. Survey of X-ray diffraction patterns of Bi–Fe-molybdate catalysts (Bi-rich region).

ber of characteristic diagrams are given in Figs. 3 and 4. They were obtained with Fe-filtered Co-radiation. The diagrams are quite complicated but they could be resolved by assuming the presence of the following phases:

(1) $Bi_2O_3 \cdot 3MoO_3$: identical in reflections to those given by Batist *et al.* (*1*). The intensity of the reflections gradually decrease with increasing Fe content.

(2) $Fe_2O_3 \cdot 3MoO_3$ closely similar to the reflections given by Fagherazzi and Pernicone (*5*) for the Fe defective state. Intensities decrease with increasing Bi content.

(3) $Bi_2O_3 \cdot MoO_3$ (Koechlinite). This pattern could only be identified in the 9Bi/1Fe sample: its reflections are marked by *o*. Reflections are identified by $d = 3.76$, 3.15, 2.74, 2.69, 1.940, and 1.920 Å.

(4) A compound that was new to us and which we shall further indicate as compound *X*. Its reflections are indicated in the figure by *x* and given in Table 2, together with those of a pattern published by McClellan (*6*) to which it bears a close resemblance.

TABLE 2
X-RAY REFLECTIONS OF COMPOUND *X*

Compound *X*		Diagram, given by McClellan (*6*)			
d (Å)	Int (rel)	*d* (Å)	Int (rel)	*d* (Å)	Int (rel)
4.88	15	4.86	3	1.73	11
4.79	20			1.60	15
3.17	95			1.57	7
3.14	100	3.14	100	1.28	3
2.90	35	2.93	18	1.27	5
2.69	10				
2.63	30	2.63	17		
2.49	5				
2.32	10	2.31	4		
1.95	25	1.95	20		
1.89	10				
1.87	10	1.86	8		

McClellan observed the pattern in a technical Bi–molybdate + H_3PO_4 on SiO_2 catalyst that was pretreated at a temperature of 750°C. The relative concentrations of the various phases as a function of the composition have been given in Fig. 5. They were

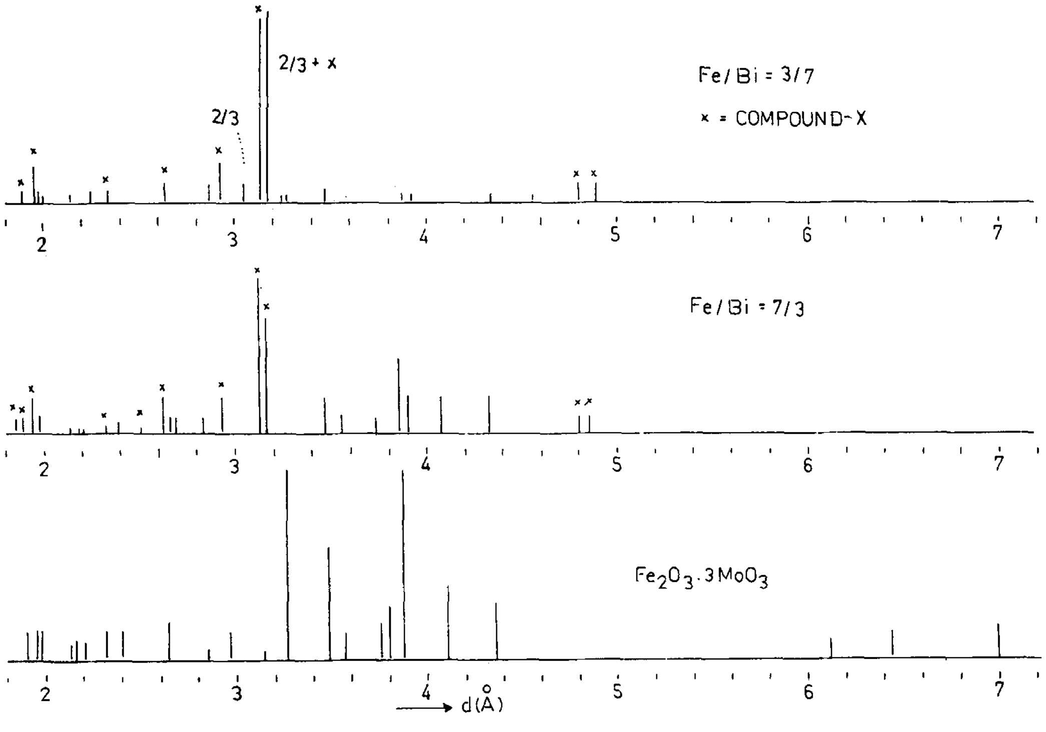

FIG. 4. Survey of X-ray diffraction patterns of Bi–Fe-molybdate catalysts (Fe-rich region).

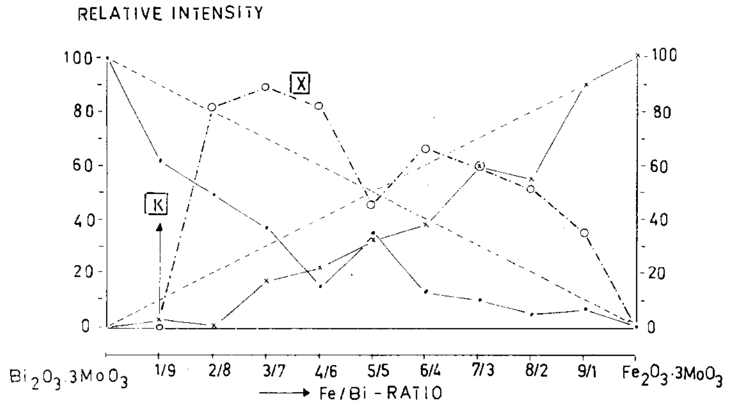

FIG. 5. Relative concentrations of various phases in the Bi-Fe-MoO_3 system.

obtained from the intensities of groups of lines characteristic for the separate phases. It is seen that the concentration of X is highest at Bi-Fe = 7/3 and 4/6 but shows a dip at Bi-Fe = 5/5. Since both the concentrations of the 2/3 Bi-Mo and Fe-Mo are observed to be smaller than would correspond with simple mixing one might derive herefrom that X contains both Bi and Fe in relation to the average mixture composition. This, however, is not reflected in a change in the line spacing.

The Bi-Fe = 5/5 sample was heated to higher temperature in order to see whether it might show higher concentrations of X. Melting at a temperature of 760°C, however, led to the complete disappearance of its lines, the sample showing only Bi-Mo and Fe-Mo = 2/3 reflections. This change was also apparent from the change in color that went from light brown to a black-green.

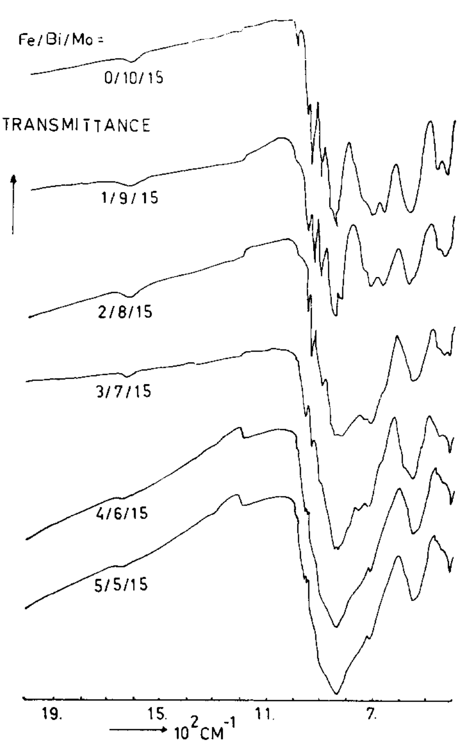

FIG. 6 Survey of infrared spectra in the Bi-Fe-molybdate system (Bi-rich region).

Infrared Absorption

The infrared spectra were obtained by the KBr disk technique with the Hitachi Model EPI-92, range 400-4000 cm^{-1}. The measurements were restricted to the Bi-Fe system. The spectra are shown in Figs. 6 and 7, where the transmittance has been plotted vs the wavenumber. Going from Bi-Mo = 2/3 to Fe-Mo = 2/3 the general impression is that of a gradual simplification of the spectra. This is mainly due to the growth of the band at 800-830 cm^{-1} that is often considered to be connected with a tetrahedrally surrounded Mo^{6+} ion. On closer inspection, this band in its growth appears originally to broaden and later to narrow again. This might be caused by the formation of a broad band between 700 and 800 cm^{-1}, a band that is characteristic of the Koechlinite structure and, as a consequence, connected to an octahedrally surrounded

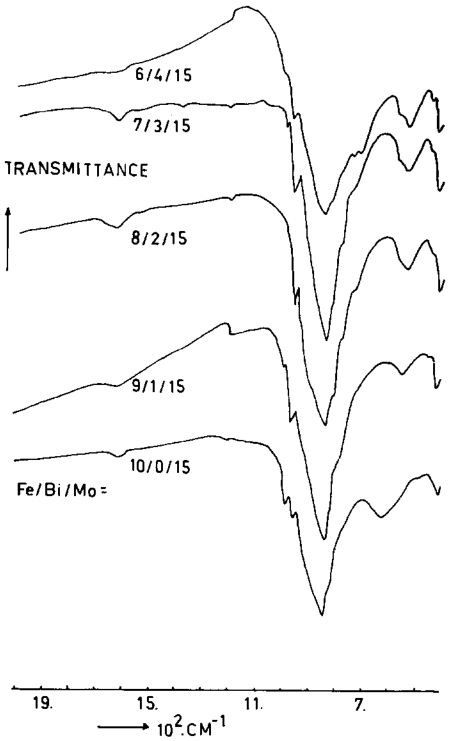

FIG. 7. Survey of infrared spectra in the Bi–Fe–molybdate system (Fe-rich region).

Mo^{6+} ion with the octahedra sharing corners. The bands between 900 and 1000 cm^{-1}, formerly connected by Batist *et al.* (*1*) with edge-sharing Mo–O octahedra disappear early in the process of replacing Bi by Fe.

To summarize, replacing Bi–Mo by Fe–Mo leads in first instance to a replacement of edge-sharing octahedra by separate tetrahedra, in good agreement with the increase in concentration of the $Fe_2O_3 \cdot 3MoO_3$ compound that is generally supposed to possess its Mo^{6+} ions in tetrahedral oxygen surroundings. It does not exclude the possibility of, in the intermediate mixtures, the formation of a compound with its Mo ions in corner-sharing octahedra.

Diffuse Reflectance

Again only the Bi–Fe sequence was investigated. The measurements were made with the Zeiss Spectrophotometer P.M.Q.II with double monochromator 1 P 28. The angle of incidence was 45° and in all cases one of the components ($Bi_2O_3 \cdot 3MoO_3$) was used as the standard of comparison. The results are given in Figs. 8 and 9.

The band edge for the charge transfer absorption is situated around 25000 cm^{-1} for Bi_2O_3–$3MoO_3$. For the Bi–Fe = 9/1 we observe that this edge is somewhat displaced to the red thus explaining the yellow color of the substance. Somewhat later in the sequence, a new band develops with its edge around 19000 cm^{-1} in agreement with a gradual change in color from yellow to brown. This band is fully developed at high Fe concentration such as Bi–Fe = 2/8 and 1/9 to disappear again for the pure Fe com-

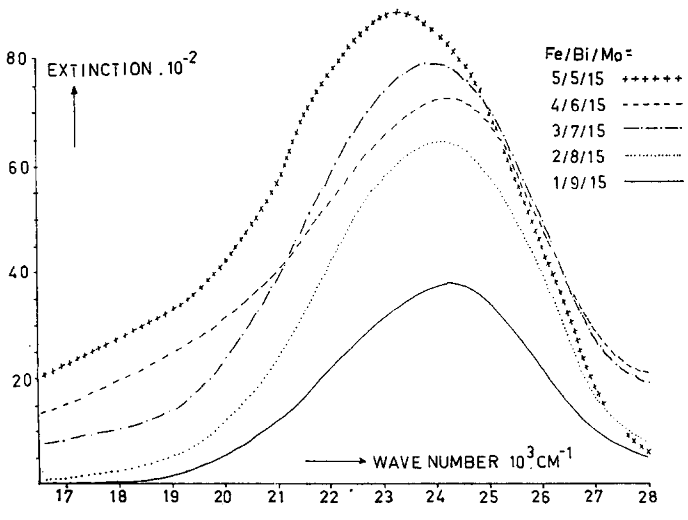

FIG. 8. Diffuse reflectancies for mixtures of Fe_2O_3–$3MoO_3$ and Bi_2O_3–$3MoO_3$ (Bi-rich).

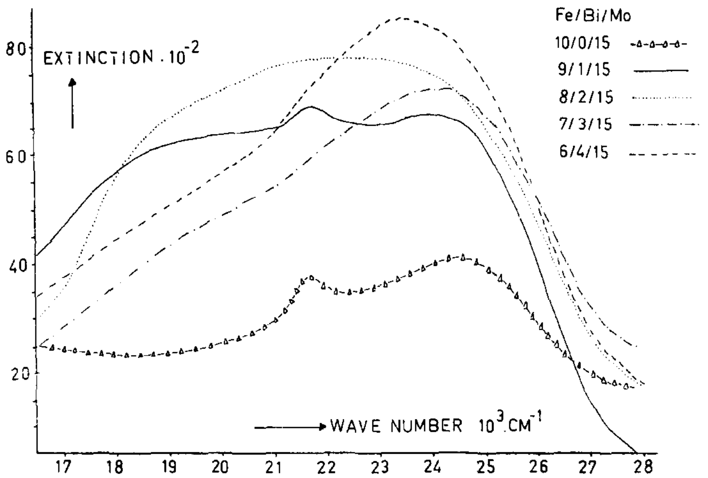

FIG. 9. Diffuse reflectancies for mixtures of Bi_2O_3–$3MoO_3$ and Fe_2O_3–$3MoO_3$ (Fe-rich).

pound, which has a different light absorption pattern.

Activity Measurements

Comparison of the activities of promoted catalysts. $Bi_2O_3 \cdot 3MoO_3$ catalysts with relatively small amounts of the promoting substances $BiPO_4$, $Fe_2O_3 \cdot 3MoO_3$, and $Cr_2 \cdot 3MoO_3$ were first compared in continuous flow experiments at different temperatures. The basis for comparison was given by the pure 2/3 compound. However, it was found in the course of the measurements that the activity of this compound is not constant in time but decreases slowly and finally settles at a remarkably low level. It is noteworthy that the catalyst in the course of this process changes its color from slightly yellow to pure white. No such change in activity was observed for the promoted samples. In the comparison with the activities of the nonpromoted samples and the variously promoted catalysts as given in Fig. 10, the activities of the fresh and aged 2/3 samples have been drawn in to allow a better check on the degree of promotion. In order not to complicate the figures, only the decrease in the butene concentration and the increase in the butadiene concentration as a function of the temperature under standard flow conditions have been given. No important changes were observed for either the isomerisation, which is found in fact to be slightly diminished by the addition of the promoters, or for the combustion, which remains substantially unchanged. It is seen that $BiPO_4$ and $Fe_2O_3 \cdot 3MoO_3$ if present in concentrations of ~10 mole % exert a pronounced promoting action while Cr_2O_3–$3MoO_3$, although undoubtedly also a promoter, is, less effective.

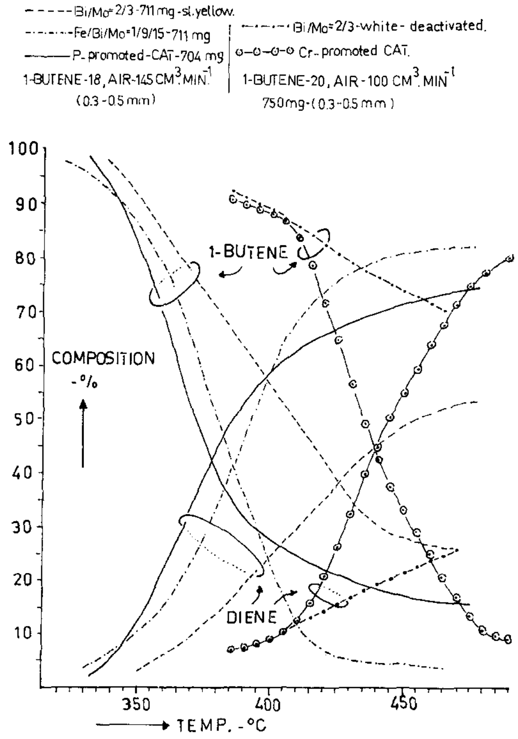

FIG. 10. Comparison of dehydrogenation activities and product distributions for Fe, Cr and P promoted catalysts and for pure $Bi_2O_3 \cdot 3MoO_3$ in continuous flow experiments.

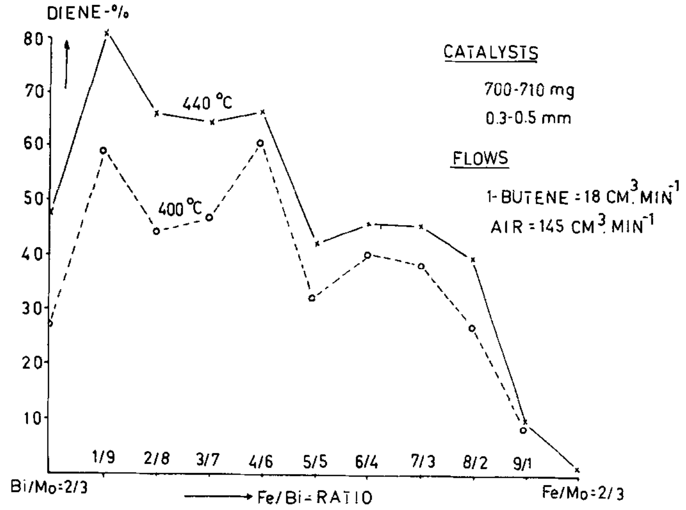

FIG. 11. Comparison of dehydrogenation activities for Bi_2O_3–$3MoO_3$–Fe_2O_3–$3MoO_3$ samples with varying Fe–Bi ratios in continuous flow experiments.

Activity in the system Bi_2O_3–$Fe_2O_3\cdot 3MoO_3$. Figure 11 illustrates the activities of samples consisting of combinations of Bi- and Fe-molybdates as a function of the Bi–Fe ratio and measured according to the continuous flow method. The activities were determined at 400 and 440°C: the samples were all freshly prepared. It is seen that the Bi–Fe = 9/1 sample is the most active but that all samples whatever their composition are more active than would correspond with mixtures of $Bi_2O_3\cdot 3MoO_3$ and the almost inactive $Fe_2O_3\cdot 3MoO_3$. Especially noteworthy is the relatively low activity of the Bi–Fe = 5/5 sample because this corresponds with the anomalous low concentration of compound X as found in the X-ray study. It is noteworthy that it appears possible to replace 80% of the Bi by Fe before the activity falls below that of the 2/3 compound.

The Kinetics of the Oxidation of 1-Butene over Promoted Catalysts

Before discussing the kinetics over promoted catalysts it is necessary to reconsider the kinetics for the unpromoted catalyst.

Kinetics of the reaction over $Bi_2O_3\cdot 3MoO_3$. Results of pulse experiments were earlier published by Keizer *et al.* (*7*) who found the reaction to be first order with respect to the partial pressure of butene and zero order for the partial pressure of oxygen. The activation energy of the reaction was calculated to be 11 kcal mole⁻¹. Adding butadiene to the feed inhibited the reaction but the effect was far smaller than observed for the 2/1 samples. These experiments were completed by additional runs under continuous flow conditions. Figure 12-A shows that the increase in conversion by an increase of the contact time i.e., by using more catalyst at constant flow rates, is in reasonable agreement with a rate expression as proposed by Adams *et al.* (*8*),

$$-dy/dt = ky \qquad (1)$$

in which y represents the concentration of butene in the reaction mixture including the presence of steam and oxygen. Plotting log k vs $1/T$ as in Fig. 12B for 1000 mg catalyst shows that a simple Arrhenius relation is obeyed with an activation energy of 12 kcal mole⁻¹ which is very near Keizer's estimate. There are only slight indications of an increase in the slope at temperatures below 400°C.

Kinetics of the reaction over the Bi–Fe–Mo = 9/1/15 catalyst. Pulse experiments were carried out with similar amounts of catalysts (1170 mg) as used by Keizer *et al.* and gas compositions of the exit gases were calculated taking into account all gases

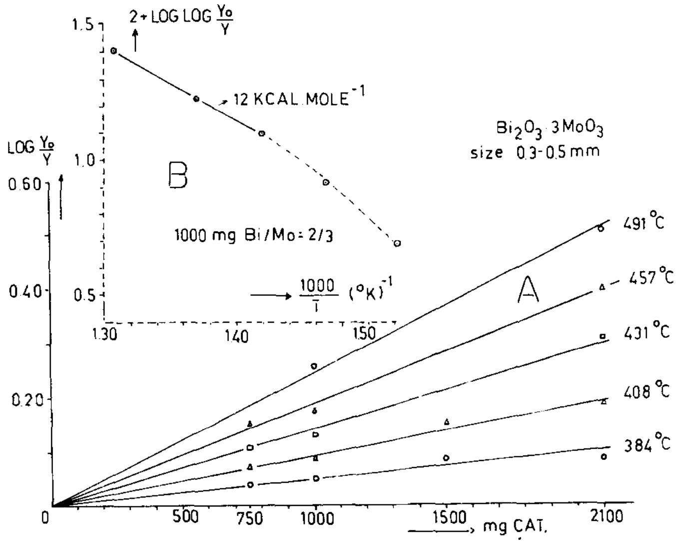

FIG. 12. (A) The first-order dependence on the partial pressure of butene in continuous flow experiments for pure $Bi_2O_3 \cdot 3MoO_3$. (B) Arrhenius plot of first order reaction constants vs reciprocal temperature for the reaction of 1-butene to butadiene in continuous flow experiments.

present. Figure 14C shows that plotting log *k*, calculated according to Eq. 1, vs 1 T produces a straight line from which an activation energy of 13 kcal mole^{-1} can be deduced. The catalyst is found to be very active and a substantial conversion is already obtained at a temperature as low as 300°C (Fig. 13A & B). At 225°C, the conversion is seen to be independent of the oxygen pressure (Fig. 14A); even in the absence of O_2, the conversion is sustained. However, increasing the butene concentration does not lead to conversions that follow Eq. 1. At relatively low partial pressures of butene the amount of butadiene produced is found to come to a constant level (Fig. 14B). The situation therefore seems similar to that encountered by Keizer *et al.* for the 2/1 catalyst.

The kinetics were accordingly also studied under *continuous flow* conditions. Figure 15A shows that the amount of butadiene produced remains constant at a constant input of butene but a varying intake of "artificial air." If the air feed is constant but the butene intake varied, the results shown in Fig. 15B are obtained. The amount of butadiene produced increases linearly with the butene intake to become constant after it exceeds a certain value.

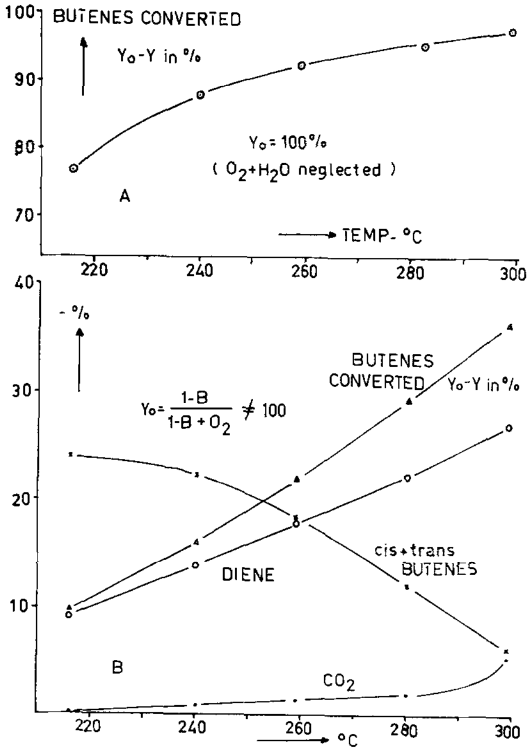

FIG. 13. (A) Conversion of butene as function of temperature in pulse experiments for the Fe–Bi–Mo = 1/9/15 catalyst. (B) The product distribution as function of temperature for the Fe–Bi–Mo = 1/9/15 catalyst.

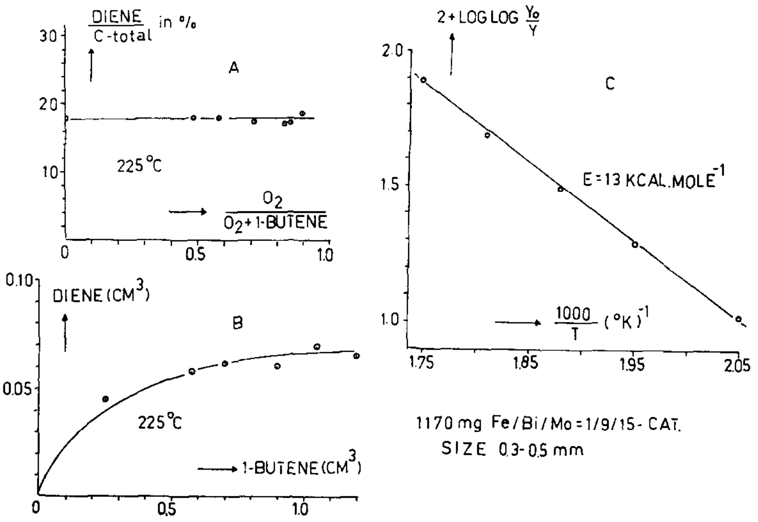

FIG. 14. (A) Determination of the oxygen order dependence on the Fe-promoted catalyst in pulse experiments: constant amount of 1-butene and varying amounts of oxygen. (B) Determination of the butene order dependence on the Fe-promoted catalyst in pulse experiments: constant amount of oxygen and varying amounts of 1-butene. (C) Arrhenius plot of first-order reaction constants vs reciprocal temperatures for the Fe-promoted catalyst in pulse experiments.

Adding butadiene to the feed produces a marked inhibition at temperatures below 400°C but the inhibition disappears above this temperature (Fig. 16A). Plotting log k vs $1/T$ leads to the result shown in Fig. 16B: there seem to exist two intersecting straight lines from which activation energies of 9–10 kcal·mole^{-1} above, and 38 kcal mole^{-1} below 400°C can be derived. The overall situation is therefore entirely similar to that reported by Batist, Prette and Schuit (*9*) for the case of the $Bi_2O_3 \cdot MoO_3$ (Koechlinite) catalyst. In other words a reaction was encountered that is of zero order in the oxygen partial pressure, probably of the first order in the butene

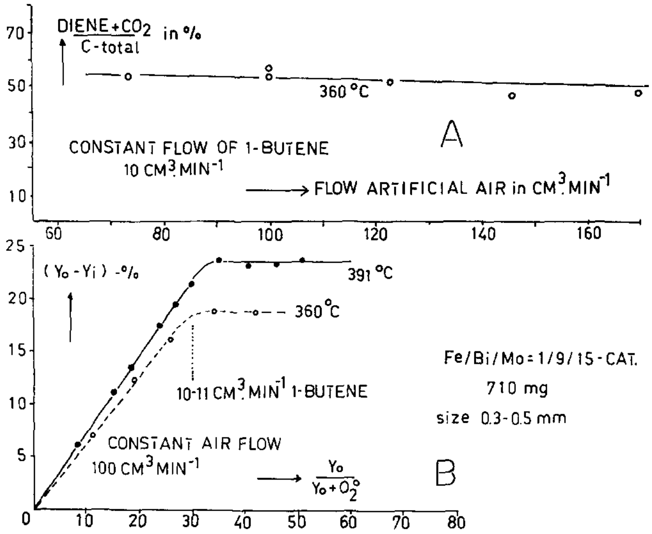

FIG. 15. Conversion of butene over the Fe-promoted catalyst in continuous flow experiments: (A) varying air input with constant butene input. (B) varying butene input with constant air input.

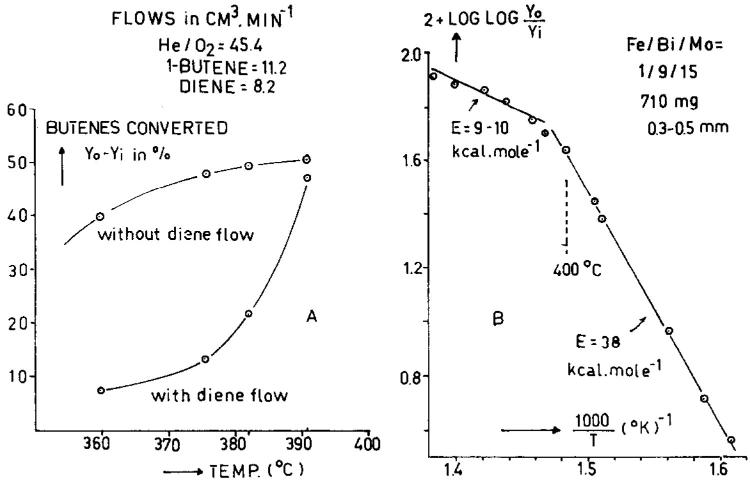

FIG. 16. (A) Inhibition by butadiene as function of temperature on the Fe-promoted catalyst in continuous flow experiments. (B) Arrhenius plot of first-order reaction constants vs reciprocal temperature in continuous flow experiments.

partial pressure and strongly inhibited by its product, butadiene, below 400°C, an inhibition that disappears above this temperature.

Adsorption on the Promoted Catalysts

Matsuura and Schuit (*10*) recently studied the adsorption of butene, butadiene, O_2 and H_2O on various Bi–Mo combinations, both in the oxidized and the partially reduced state. The adsorption isotherms for the organic substances and for H_2O are simple Langmuir isotherms that are either single site (SS) or dual site (DS). This enabled the particular adsorption to be characterized by three parameters, the heat of adsorption Q, a constant with the dimension of a pressure $p_0{}^0$ and finally the maximal volume of adsorption V_m. Significant variations in these constants were found to occur when comparing one type of adsorption for the various Bi–Mo compounds. Oxygen was only found to be adsorbed at partially reduced samples while a fully oxidized sample was found to dissociate O_2 in a reversible process, the properties of which were again determined by the nature of the Bi–Mo compound. Partially reduced samples sorb oxygen but the reoxidation of the sample was found to occur in steps. At room temperature, there exists a limited but fast sorption. Increasing the temperature leads to the coming into existence of a process that is independent of the pressure of the gas, its characteristics being that of a diffusional transport in the bulk. Finally, at temperatures above 400°C a new reaction comes to the fore; that is found to be first order in the oxygen pressure. Also for the reoxidation, it proved possible to define the reaction by a small number of parameters such as: volume adsorbed at room temperature, the constant of diffusion and its temperature coefficient and finally the rate constant and its activation energy of the high temperature reaction. Since a study of adsorption appeared to produce considerable information concerning the state of the surface of an oxidation catalyst, it was decided to perform similar experiments on promoted catalysts of the type discussed here.

Dissociation of O_2 from Promoted Catalysts

The samples were heated to 460°C under O_2, cooled to room temperature in an oxygen atmosphere after which they were evacuated to 10^{-5} mm. The temperature was subsequently increased at a rate of 2.5°C min^{-1} and the pressure in the reaction vessel determined as a function of the temperature. The results for some samples are shown in Fig. 17. It is seen that the disso-

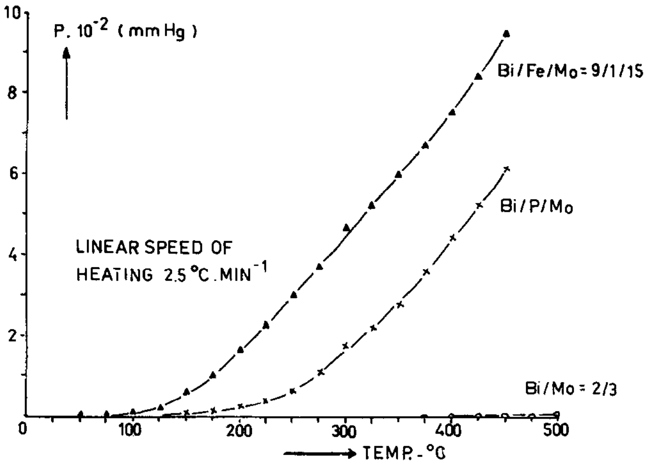

FIG. 17. Oxygen dissociation as function of temperature for Fe- and P-promoted catalysts and for pure Bi_2O_3–$3MoO_3$.

ciation starts at temperatures that are considerably lower for the promoted catalysts than for the nonpromoted 2/3 sample. The tendency to dissociate O_2 for the promoted catalysts even surpasses that of the 2/1 sample.

Re-Oxidation of Reduced Samples

As examples of the results for the various samples it is shown in Fig. 18 that a P-promoted catalyst that was reduced for 0.75% (i.e., in which 0.75% of the O atoms were removed by a previous reduction by butene) sorbs O_2 in the temperature range below 400°C in a similar way as the samples investigated earlier (*10*). The amount sorbed increases linearly with the square root of the time and the rate-determining process can therefore be considered as a diffusion in the bulk. It is shown in Fig. 19 that above 400°C the sorption is first order in the oxygen pressure. Similar results were obtained for the Bi–Fe = 9/1 sample (Fe-

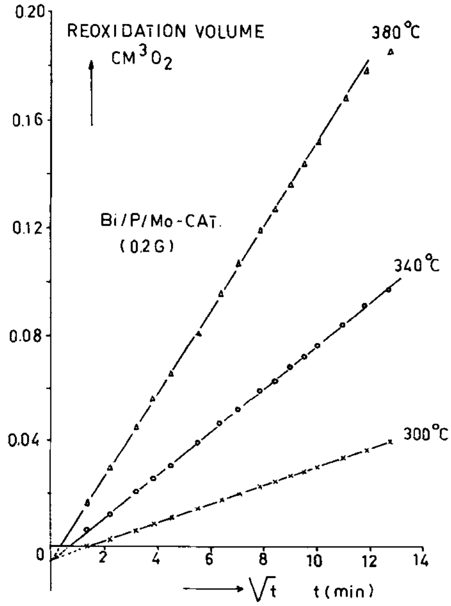

FIG. 18. Reoxidation rates of a 0.75% reduced catalyst at temperatures <400°C.

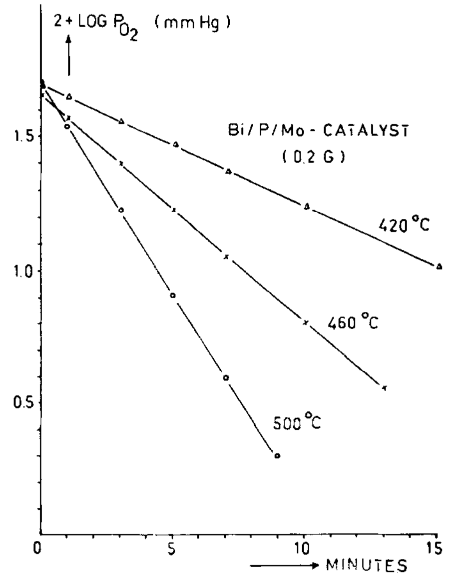

FIG. 19. Reoxidation rates of a 0.75% reduced catalyst at temperatures 420–500°C.

TABLE 3

PARAMETERS FOR THE REOXIDATION RATES OF REDUCED CATALYST SAMPLES

	High temperatures (420–500°C)			Low temperatures (300–380°C)	
Catalyst	% O red	$\log k_0$ (min^{-1})	E (kcal mole^{-1})	$\log B_0$	E (kcal mole^{-1})
P-promoted	0.75	4.79	16.1	6.64	26.7
Fe-promoted	0.75	4.29	14.2	6.37	26.7
Bi–Mo = 2/3	0.75	6.64	23.6	3.37	28.2
Bi–Mo = 2/1	0.50	4.83	16.9	6.77	27.4
B_0 ($\mathrm{cm}^6\ \mathrm{min}^{-1}\ \mathrm{g}^{-2}$)					

promoted catalyst). The parameters for the rate processes are given in Table 3. See Matsuura and Schuit (*10*) for the meaning of the parameters.

Attention is drawn to the fact that the parameters for the promoted samples deviate sharply from those of the nonpromoted sample but approach those given by Matsuura and Schuit for the 2/1 catalyst.

Adsorption of 1-Butene

The adsorption was measured as a function of pressure and temperature for both promoted and nonpromoted catalysts and for two different types of pretreatment, viz (A) the "oxidized" state, the sample was heated in O_2 at 460°C, cooled under O_2 to room temperature and subsequently evacuated to 10^{-5} mm. (B) the "evacuated" state: the sample was heated under O_2 at 460°C, evacuated to 10^{-5} mm at this temperature for 10 hr, cooled under pumping to room temperature.

The different manners of pretreatment did not produce different results and the adsorption isotherms measured were found to be substantially the same. One example of a series of measurements is given in Fig. 20 (P-promoted catalyst). It is seen that the adsorption follows a dual site Langmuir isotherm. The parameter for the adsorption processes for the various samples are given in Table 4. For the meaning of the parameters see Matsuura and Schuit (*10*).

As seen from the table, the promotion of the 2/3 catalyst by the various promoters is equivalent to a substantial increase in the number of adsorption sites. However, judging from the adsorption parameters such as Q and p_0^0, the character of the sites remains the same.

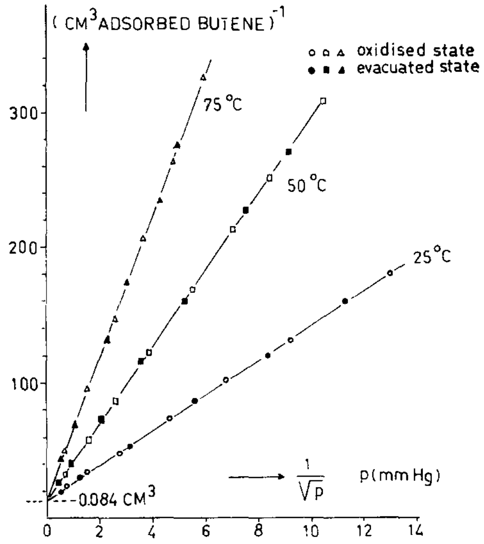

FIG. 20. Adsorption–desorption equilibria of 1-butene on P-promoted catalyst in the "oxidized" and in the "evacuated" state.

TABLE 4

PARAMETERS FOR THE ADSORPTION EQUILIBRIA OF 1-BUTENE OVER VARIOUS CATALYSTS

Catalyst	Sat ads vol ($\mathrm{cm}^3\ \mathrm{g}^{-1}$)	$\log p_0^0$ (mm)	Q (kcal mole^{-1})
P-promoted	0.084	9.17	12.4
Fe-promoted	0.42	9.14	12.0
Bi–Mo = 2/3	0.013	9.19	11.9
Bi–Mo = 2/1	0.100	9.46	11.8

Adsorption of Butadiene

As found previously (*10*), butadiene can adsorb in two essentially different ways: (1) a fast and "weak" adsorption that follows a dual-site type of Langmuir isotherm and that possesses a similar maximal adsorption volume as 1-butene and (2) a slow and "strong" adsorption that follows a single-site Langmuir isotherm. The two types could only be distinguished on the 2/1 catalyst. For other samples where the adsorption is considerably smaller in volume, no distinction proved possible. The "oxidized" samples of the promoted catalysts show a similar behavior as the 2/1 sample in the previous study: also here it proved possible to separate a "weak" and a "strong" adsorption with parameters, similar to those given earlier. However, the "evacuated" samples did not produce the "strong" adsorption. In both cases, the "weak" adsorption proved to be of the dual-site type and moreover equal in volume of maximal adsorption, Fig. 21. The "strong" adsorption on the "oxidized" samples was shown to obey a single-site adsorption, (Fig. 22). The parameters of the adsorption-equilibria on the various samples are given in Table 5. For the meaning of the parameters see Matsuura and Schuit (*10*).

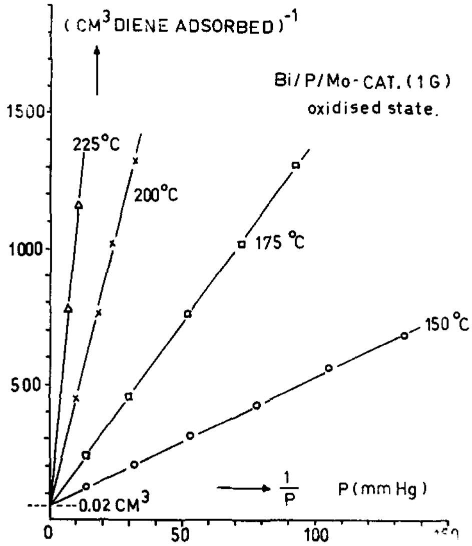

FIG. 22. Adsorption–desorption equilibria of butadiene at higher temperatures on P-promoted catalyst in the "oxidized" state.

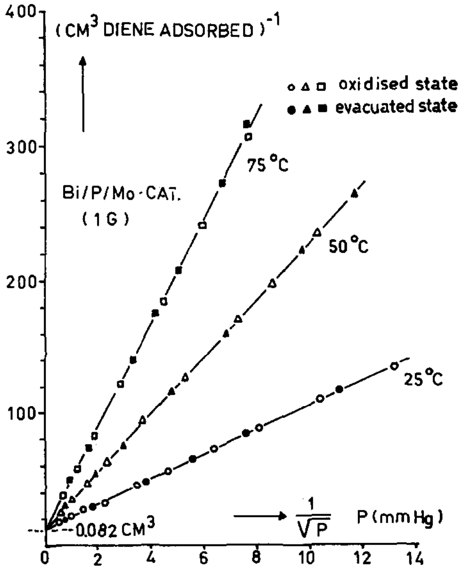

FIG. 21. Adsorption–desorption equilibria of butadiene at low temperatures on P-promoted catalyst in the ' oxidised" and in the "evacuated" state.

It is noteworthy that the strong adsorption, absent on the nonpromoted catalyst, is observed again on the promoted samples. Its properties appear similar to those of the 2/1 sample. The observations on the weak adsorption confirm those arrived at in the study of the 1-butene adsorption: the maximal volume of adsorption is strongly increased by the promotion but the site characteristics remain the same.

TABLE 5

PARAMETERS FOR THE ADSORPTION EQUILIBRIA OF BUTADIENE ON VARIOUS CATALYSTS

Weak Adsorption (25–75°C)

Catalyst	Sat ads vol (cm^3 g^{-1})	log $p_0{}^0$ (mm)	Q (kcal mole^{-1})
P-promoted	0.082	7.23	10.2
Fe-promoted	0.45	7.03	9.9
Bi–Mo = 2/1	0.112	6.62	9.2

Strong Adsorption

Catalyst	Sat ads vol (cm^3 g^{-1})	log $p_0{}^0$ (mm)	Q (kcal mole^{-1})
P-promoted	0.02	7.80	17.1
Fe-promoted	0.01	7.97	16.9
Bi–Mo = 2/1	0.024	6.81	19.4

DISCUSSION

The problem attacked in this investigation was to find an explanation for the experimental observation that some substances, if added to the Bi–Mo catalyst in relatively small concentrations, lead to a substantial increase in the activity of this catalyst without, however, decreasing its selectivity. We have indeed confirmed the existence of this promoter effect in this work and we think that we have found a solution for their action. However, while engaged in this activity, we encountered a number of interesting phenomena that should be considered separately. We shall therefore divide the discussion into two parts, that connected with the promoter action proper and another that is concerned with the other effects.

The catalyst $Bi_2O_3 \cdot 3MoO_3$ assumed in our work as a proper base for studying the promoter effects has been found to be only moderately active. Moreover, it has been shown that the activity of fresh samples is not representative of the activity of the pure compound but may be due to some extent to the presence of small concentrations of other Bi–Mo phases, probably $Bi_2O_3 \cdot MoO_3$ (Koechlinite). Evidence supporting this assumption is the decrease in activity in the course of time connected with a change in color from slightly yellow to white, a change that is known to occur if small concentrations of the 2/1 phase are eliminated (Batist *et al.* (*1*)). The explanation proposed now for the existence of a promoter action by such widely different substances as $BiPO_4$, $Fe_2O_3 \cdot 3MoO_3$, and $Cr_2O_3 \cdot 3MoO_3$ is that their action is given by the fact that they all tend to increase the 2/1 concentration in the 2/3 catalyst. This explanation is based on the following observations:

(1) The presence of the 2/1 phase was indeed proved by an X-ray study for the case of the addition of $BiPO_4$ and of $Fe_2O_3 \cdot 3MoO_3$.

(2) Additional confirmation of the presence of the 2/1 compound was found for the case of $Fe_2O_3 \cdot 3MoO_3$, where the presence of 10 mole % of this substance leads to a shift in the charge transfer absorption band to a position that agrees with the presence of the 2/1 compound. The yellow color of the Fe–Bi = 1/9 compound is therefore not caused by the presence of the Fe-molybdate that possesses a different absorption spectrum but to that of the 2/1 compound.

(3) The kinetics of the reaction, in particular the inhibition by the product butadiene, have been shown to change from a behavior characteristic for the 2/3 catalyst where inhibition by butadiene is only slight to that encountered in an earlier study [Batist, Prette and Schuit (*9*)] for the 2/1 catalyst to which it became very similar. In particular the strong inhibition by butadiene and the consequent increase of the activation energy to the high value of 38 kcal $mole^{-1}$, characteristic for the conversion over the 2/1 catalyst, were also encountered in the 2/3 samples, promoted by Fe.

Similar changes in properties have been observed in the adsorption of the catalyst where butene and butadiene are concerned. It has been shown in an earlier paper by Matsuura and Schuit (*10*) that the 2/1 catalyst possesses two different adsorption centers, the simultaneous presence of both being necessary for the catalytic action. One of these, the A center, was shown to be an oxygen ion of special properties which furnishes the opportunity to attach the H atoms dissociated during the oxidation and which is also the site from which the resulting water molecule leaves the reaction. In the 2/1 catalyst it has the additional property of being able to adsorb butadiene in a slow but "strong" adsorption, thus explaining the inhibition by butadiene. Another center, named the B center, serves to adsorb the olefin which is to be converted. Now, in going from the 2/1 catalyst to the 2/3 catalyst the number of B centers undergoes a drastic decrease without changing their specific properties. On the other hand the concentration of the A centers, although also somewhat decreased, remains essentially the same but their properties change substantially. In particular they lose their property to adsorb butadiene. The relevant observation from the present investigation was that for the $BiPO_4$- and Fe-molybdate promoted catalysts the concentration of the B centers was found to be substantially increased in comparison to that on the 2/3 catalyst although again their specific properties were not altered. Moreover, simultaneously the A centers regained their property to adsorb butadiene in the "strong" form in excellent agreement with the kinetic observation that the reaction becomes inhibited by butadiene.

The combination of all these observations makes it highly probable that to a first approximation the promoter action is caused by a single effect, viz, an inhibition of the formation of the pure 2/3 compound in favor of a formation of the 2/1 compound. To a considerable extent this also explains why the action of different promoters is so similar in their result. However, there are some observations that seem to show that there may be other factors coming into play.

The first object that shall concern us is finding of compound *X* in the system $Bi_2O_3 \cdot 3MoO_3$–$Fe_2O_3 \cdot 3MoO_3$. In view of the fact that the existing knowledge on the structures of the two molybdates leads one to believe that they were essentially different, it was thought that they would not show solid solutions. This was indeed confirmed by the observation that the positions of their characteristic reflections when compared to the data given by Batist *et al.* (*1*) for the Bi–Mo compound and by Fagherazzi and Pernicone (*5*) for the Fe-defective Fe–Mo compound were substantially unchanged. However, it now appears that their simultaneous presence leads to the formation of a new phase. It is an interesting observation that this phase can also occur in Bi–Mo systems without Fe as shown by McClellan (*6*) (we have to thank Dr. Ir. J. C. van Hooff for attracting our attention to this fact). So far, the compound has never been observed in our pure Bi–Mo samples and it therefore appears that it can only come into existence if there are other compounds that stimulate its presence. Although it is definitely less active than the 2/1 Bi–Mo compound it exceeds the 2/3 compound in activity to a considerable degree as shown for instance by the fact that the Fe–Bi = 2/8 sample is more active than the pure 2/3 phase. Moreover, this increase in activity is not connected by a loss in selectivity. It is therefore a compound worthy of further discussion.

Knowledge about the properties of compound *X* is somewhat restricted at this moment. According to McClellan its structure is related to the Scheelite structure which appears in agreement with infrared information that indicates a tetrahedral surrounding of the Mo^{6+} ion. The X-ray diagram suggests a tetragonal cell but the diagrams presently available are too vague to be certain of this point. From the fact that it exists in what seem to be considerable quantities over the whole range of Bi–Fe ratios it is difficult to avoid the conclusion that Bi^{3+} and Fe^{3+} ions can replace each other in the structure and the typical brownish color of the compound in the Fe-rich regions, probably connected with the strong band at 19000 cm^{-1}, therefore might be used to study the surrounding of the Fe ion and consequently also of the Bi ion in the crystal. One of the interesting details in its properties is that its activity decreases, although only to a relatively small extent, by going over from the Bi-rich to the Fe-rich side. The difficulty in studying compound *X* is largely given by the fact that so far we have not succeeded in obtaining it in pure form. In all our samples it was present next to the Bi–Mo and the Fe–Mo compounds. We intend, however, to study its properties in more detail.

The next item in our discussion will be devoted to some details in the adsorptive properties that may perhaps be connected with the presence of *X*. While most of the observations in connection with the adsorptive properties of promoted catalysts can be related directly to the presence of the Koechlinite (2/1) phase there is one observation that indicates a more profound change. All the promoted samples investigated so far show a considerably enhanced tendency to dissociate O_2, a tendency that surpasses even that of the 2/1 phase. This is a detail of considerable relevance in connection with the deductions made by Matsuura and Schuit (*10*). Their proposal that the center which is active in the catalytic oxidation is a combination of an A center and a B center is confirmed by the present results which show that the increased activity of the promoted catalysts runs parallel with an increase in the concentrations of *both* centers. The properties of the B centers are not affected by this increase but the situation regarding the A centers may be different. It was also postulated that this A center is an oxygen ion in the catalyst structure with special properties such as the ability to adsorb butadiene. This has been confirmed in a striking manner in the present investigation: a catalyst that possesses the property to adsorb butadiene in the "strong" type of adsorption loses this property if it has been evacuated at 460°C. This is not the case for the sites that adsorb butene: A previous evacuation at higher temperatures leaves the adsorptive properties for this substance unaltered which clearly shows that the two sites are indeed different. However, since this experiment shows that some of the surface oxygens do possess special properties (since they can be removed by pumping at 460°C) they should also be identical to those that become dissociated at a lower temperature by heating in a vacuum. We have shown that precisely those oxygens are more easily dissociated from the promoted catalysts than from the 2/1 phase. Apart from the proven conversion of the 2/3 sample to the 2/1 modification there must, accordingly, exist still another factor that has to be taken into account. The obvious conclusion is that systematic research should be performed concerning the tendency of catalysts to dissociate O_2. This is evidently not a particularly original suggestion. The new feature introduced here is that such a study will have to be combined with an investigation into the connection between this tendency for dissociation and the adsorptive properties of the catalyst towards olefins and butadiene.

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REFERENCES

1. BATIST, PH. A., DER KINDEREN, A. H. W. M., LEEUWENBURGH, Y., METZ, F. A. M. G., AND SCHUIT, G. C. A., *J. Catal.* **12,** 45 (1968).

2. U. S. Patent 2, 904, 580 Standard Oil Company, Cleveland, Ohio (1959).

3. KAMRAN AYKAN, *J. Catal.* **12,** 281 (1968).

4. VOGE, H. H., ADAMS, C. R., U. S. Patent **2,** 991, 321 (1961).

5. FAGHERAZZI, G., AND PERNICONE, N., *J. Catal.* **16,** 321 (1970).

6. MCCLELLAN, W. R. in U. S. Patent 3, 415, 886 (1968).

7. KEIZER, K., BATIST, PH. A., AND SCHUIT, G. C. A., *J. Catal.* **15,** 256 (1969).

8. ADAMS, C. R., VOGE, H. H., MORGAN, C. Z., AND ARMSTRONG, W. E., *J. Catal.* **3,** 379 (1964).

9. BATIST, PH. A., PRETTE, H. J., AND SCHUIT, G. C. A., *J. Catal.* **15,** 281 (1969).

10. MATSUURA, I., AND SCHUIT, G. C. A., *J. Catal.* **20,** 19 (1971).