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The Catalytic Oxidation of 1-Butene over Bismuth Molybdate Catalysts

II. Dependence of Activity and Selectivity on the Catalyst Composition

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The dependence on the composition of the oxide catalyst of the rate and selectivity of the oxidative dehydrogenation of 1-butene to butadiene over Bi_2O_3—MoO_3 catalysts has been investigated. The rate appears to be mainly determined by the Bi/Mo ratio and is optimal at Bi/Mo = 1. This optimal composition is not connected with the presence of a particular compound in the binary oxide system: all compounds identified so far are either less active or not active at all. The activity pattern is complicated by a sintering reaction that differs in intensity in various ranges of the composition. The selectivity is mainly decided by the occurrence of the double-bond isomerization. This is more developed at lower temperatures and in the MoO_3-rich compositions. It is considerably inhibited by a high-temperature pretreatment of the catalyst.

The promoter action of Bi^{3+} is explained by the assumption of an enhanced tendency to dehydroxylation of the surface, thereby leading to the formation of anion vacancies that serve to accept the intermediate allylic structure. Formation of this structure is further assumed to be possible only if it becomes π bonded to Mo, thus explaining the advantage of the simultaneous presence of Bi and Mo.

INTRODUCTION

In a former paper [Bleyenberg, Lippens, and Schuit, ref. (*1*)] a report was presented concerning the phase relations in the Bi_2O_3–MoO_3 system. This served as a prelude to an investigation concerning the connection between rate and selectivity of olefin oxidation reactions on the one hand and the composition of the catalyst on the other hand. The present paper deals with the oxidative dehydrogenation of 1-butene to butadiene on the catalyst system mentioned. The reaction on $Bi_2O_3 \cdot 2\ MoO_3$ catalyst was earlier discussed in some detail by Adams, Voge, Morgan, and Armstrong (*2*). They report it to proceed quite selectively in the range 350–500°C. Apart from butadiene, *cis*- and *trans*-2-butene are formed in concentration ratios that are near to one; with increasing temperature the 2-butenes formed decrease in importance. If subjected as such to the action of O_2 over the catalyst mentioned *cis*- and *trans*-2-butene are found to be less reactive than 1-butene while isomerization by double-bond shift is not rapid. A small amount of furan and of CO_2 and CO was also observed to be formed. The reaction was found to be first order in olefin and independent of oxygen and products in its rate, the activation energy being 26 kcal $mole^{-1}$. This simple relationship might be derived from a more complete kinetic expression, as given earlier by Adams (*3*)

$$\text{rate} = kp_{\text{olefin}} \frac{k_1^{1/2} p_{O_2}^{1/2}}{1 + k_1^{1/2} p_{O_2}^{1/2} + k_2 p_{\text{butadiene}}} \tag{1}$$

Evidently this rate equation reduces to the simple first order law, if

$$k_1^{1/2} p_{O_2}^{1/2} \gg 1 + k_2 p_{\text{butadiene}}$$

Also the order of the oxidation of propene to acrolein is reported by Adams *et al.* to be first order in the hydrocarbon pressure and independent of oxygen and products over the bismuth molybdate catalyst.

Under circumstances, however, the rate equation seems better represented by a zero order dependency on the partial pressure of the hydrocarbon as was found by Margolis, Malyarova, and Roginskii (*4*) for oxidation of propene on V_2O_5 at temperatures between 360° and 430°. [See also Margolis, Plyshevskaya (*5*).]

The potential activity and selectivity of catalysts were related by Sachtler and de Boer (*6*) to the strength of the metal–oxygen bond. If this bond is strong the number of oxygen anion vacancies able to bind the olefin is relatively low, but the postulated intermediate allyl radical can be readily converted to either a diene or an unsaturated aldehyde. The activity therefore will be small but the selectivity excellent. If on the contrary, the metal–oxygen bond is weak there will be plenty of anion vacancies and hence a considerable activity. However, reaction leading to the normal end products might be difficult and the selectivity therefore is believed to be low.

Experimental Procedures

Preparation of the catalysts used. The samples tested for their activity consisted of three series.

(A) The samples as discussed by Bleyenberg *et al.* (*1*). They were prepared by heating mixtures of Bi_2O_3 and MoO_3 at 600°C, grinding, and repeated firing. The samples vary in composition from 100 Mo to 100 Bi in stepwise increases of 5% (atomic ratio).

(B) Samples prepared by mixing $Bi(NO_3)_2 \cdot 5H_2O$ p.a. and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ p.a. in powdered form, evaporation of hydrate water, and heating to decompose nitrate and ammonia, cooling, powdering, and calcining in air at 600°C during 20 hr. Compositions of various samples are recorded in Table 1.

(C) Samples prepared as under (B) but with a calcination temperature of 500°C (for the composition see Table 2). A comparison with the activity of pure MoO_3 was obtained from experiments in which a Merck p.a. commercial product was preheated at temperatures of 600°C or 500°C.

TABLE 1
COMPOSITION OF SAMPLES B AND RESULTS FROM MERCURY POROSITY MEASUREMENTS[a]

Composition, Atomic ratio Bi/Mo	Mercury porosimeter data	
	Surface area ($m^2 g^{-1}$)	Pore volume of powder ($cm^3 g^{-1}$)
80/20	—	—
67/33	—	—
62/38	—	—
57/43	0.23	0.19
53/47	—	—
50/50 (a)[b]	—	—
50/50 (b)[b]	0.18	0.23
48/52	0.26	0.16
46/54	—	—
44/56	0.23	0.23
43/57	—	—
40/60	0.22	0.14
37/63	—	—
35/65	—	—

[a] Mercury porosimeter data were obtained with 1000 atm maximum pressure.

[b] See text.

Reference to the various samples will be made by giving their composition in atomic percentages Bi/Mo preceded by the symbol A, B, or C. If more than one sample of equal composition and pretreatment method was tested this will be indicated by adding the letter a, b, etc. Hence B-50/50b means that a second sample of composition Bi/Mo = 50/50 and pretreatment temperature of 600°C was prepared subsequent to an earlier preparation (a).

TABLE 2
COMPOSITION OF SAMPLES C

Atomic ratio Bi/Mo:	35/65	40/60	44/56	48/52	50/50	57/43	67/33

The surface areas of the various samples as determined by the conventional BET method proved to be very low and of the order of 1 m^2 g^{-1} or lower. For some B samples this observation was confirmed by mercury penetration measurements, the data obtained being reported in Table 1.

For some C samples, i.e., 40/60, 50/50 and 67/33 X-ray data were obtained. These were compared with those reported earlier for the A sample by Bleyenberg *et al.* There are no intrinsic differences between the two types of samples as to the phases that could be identified by X-ray. Both samples consist of a mixture of the compounds $Bi_2O_3 \cdot 3MoO_3$ and $Bi_2O_3 \cdot MoO_3$, which possess a limited mutual solubility. Intensity differences and slight shifts in the positions of some lines point to small differences in the compositions of the solid solutions. However, the differences between the two types of preparations as far as structure is concerned appear to be small.

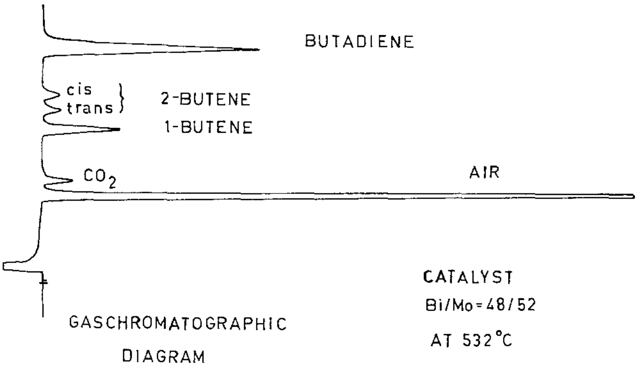


FIG. 1. Gas chromatogram of reaction products from oxidation of 1-butene.

Apparatus for testing the activities of the catalysts. The apparatus applied consisted of a microreactor connected to a gas-liquid chromatography analysis system. The microreactor is formed by a quartz tube, inside diameter 0.35 inch, fitted with a central thermowell of 0.12 inch with a movable thermocouple of chromel alumel. A small concentric furnace was fixed in such a way that color changes of the catalyst during reaction could be observed by moving the furnace up and down. The length of the fixed catalyst bed was about 3 cm.

Before experiments were started with 2.5 g of catalyst, it was ascertained that no perceptible thermal cracking and oxidation occurred in the quartz microreactor at temperatures below 630°C even when the reactor was filled with quartz powder.

Experimental conditions. All the data obtained were at atmospheric pressure. No appreciable pressure head was built up if the bed was loosely packed and the catalyst material taken was not too fine a powder. The feed rate of air and 1-butene regulated by flow meters was kept constant during all our experiments. The air/1-butene ratio was 85/20 and there was therefore an excess of oxygen. The gas velocity was 105 cm^3 min^{-1} (GHSV = 4200). An air-cooled condensor was connected to remove water and traces of other liquids before the gases were analyzed.

Analysis. A Becker gas chromatograph with heat conductivity detection was used for the analysis of the gases. By using a sampling valve, samples of 0.87 cm^3 were periodically withdrawn from the exit gases and injected into a 6-meter column filled with 10% by weight 2.4 dimethylsulfolane on Chromosorb of 30–50 mesh to separate butenes, butadiene, and CO_2.

Hydrogen was used as the carrier gas. An example of a gas chromatographic diagram is represented by Fig. 1. By using a second sampling valve and a column filled with Davison silica gel, a separation of air and CO became possible.

Generally it was found that at temperatures up to 550°C the CO formation was considerably lower than the CO_2 formation. At temperatures higher than 580°C the CO formation increases considerably. In our further discussion CO formation is neglected.

It was also checked that no isobutene was formed during isomerization and oxidation of 1-butene. For the detection of this compound a 2-m column with silver nitrate and benzyl cyanide and a 4-m column with dimethylsulfolane were used.

RESULTS

Before discussing the data relevant to the activity and selectivity measurements some observations have to be mentioned. Some of the catalysts show a yellow color that is developed especially in the 60/40 to 40/60 region of Bi/Mo atomic ratios. This color is particularly noticeable in the C series. There are some indications that a heat pretreatment at a higher temperature causes the sample to become less strongly colored, an observation especially valid for the 50/50 sample.

The onset of the reaction is usually accompanied by a temperature rise in the reactor bed. If the temperature at the start of the experiment remains below a certain level the rise is more or less homogeneous over the bed but for some samples the formation of a temperature peak is observed if the temperature at the start exceeds this level.

Temperatures recorded are those observed while the reaction was in progress. No data are reported for runs with pronounced temperature peaks. The color of the catalyst sample becomes somewhat more grayish during the reaction. For those samples in which temperature peaks develop (C series with excess of MoO_3, e.g., C-40/60 and MoO_3 pretreated at 500°C) the catalyst becomes black in the high-temperature zone. This leads to simultaneous deactivation of the catalyst as shown by a subsequent displacement of the temperature peak versus the outlet. The catalyst can, however, be regenerated by air treatment.

Activity and selectivity of the various samples were determined at several temperatures and constant GHSV.

The results are given in Figs. 2–4.

Figure 2 shows the conversion over the A series at the temperature of 555°C. This series proves less active than the others, as observable from the relatively high temperature needed to obtain satisfactory conversions. The appearance of the activity versus composition curve is rather irregular. Activity seems to be restricted to the range Bi/Mo = 40/60 to 70/30 but there appear to exist samples with low activity even in this region (see in particular A-50/50). The compounds $Bi_2(MoO_4)_3$ and $(BiO)_2 \cdot MoO_4$ are found to be only slightly active.

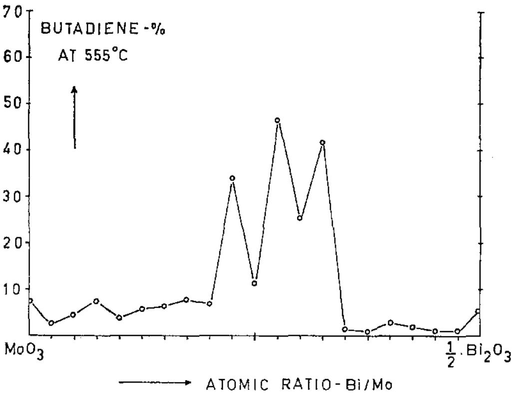


FIG. 2. Activity versus Bi/Mo compositions for oxidation of 1-butene to butadiene. Catalysts used are the A series at the temperature of 555°C.

Figure 3 shows similar results for the B series, now thereby showing their superior activity at 460°C. Apart from the level of activity the similarity with the former figure is evident. Also here the pronounced dip at the 50/50 composition is observed. There is a certain irreproducibility of the measurements in this range, the B-50/50b catalyst being somewhat more active than the B-50/50a sample (conversion 26% versus 15%). However, the general appearance of low activity persists.

Figure 4 presents the conversions for the C series at 460°C. The most active com-

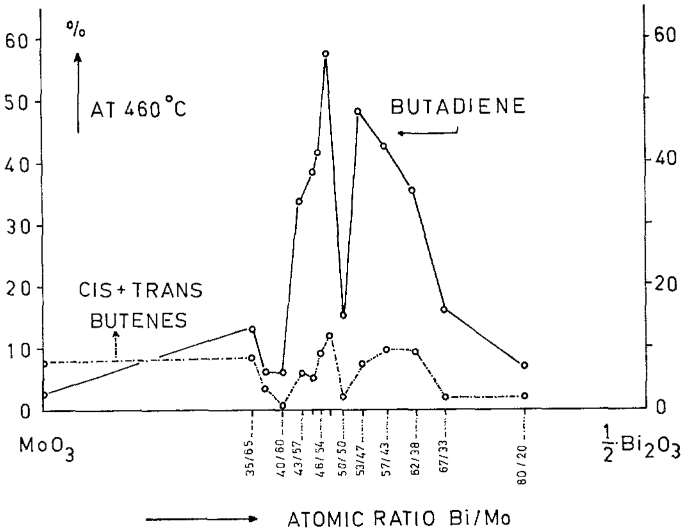


FIG. 3. Activity versus Bi/Mo compositions for oxidation of 1-butene to butadiene. Catalysts used are the B series at 460°C.

position of the B series B-48/52 is seen to be about as active as its counterpart in the C series. However, all the other samples of the C series are more active. The activity dip at the 50/50 point has disappeared. There is, furthermore, an extension of the range of active compositions versus the molybdenum-rich side while the samples with Bi/Mo > 1 are also more active, although the pattern in activity remains the same here.

As concerns the *selectivity* (see Table 3) this is determined by the occurrence of two side reactions, i.e., the conversion to CO_2 and that to *cis*- and *trans*-2-butene. The former reaction remains insignificant if the temperatures are not excessively high. The second reaction proved to be dependent on temperature, catalyst composition, and pretreatment. Higher reaction temperatures produce lower 2-butene yields. For instance, in the B series we find a yield over 86% in

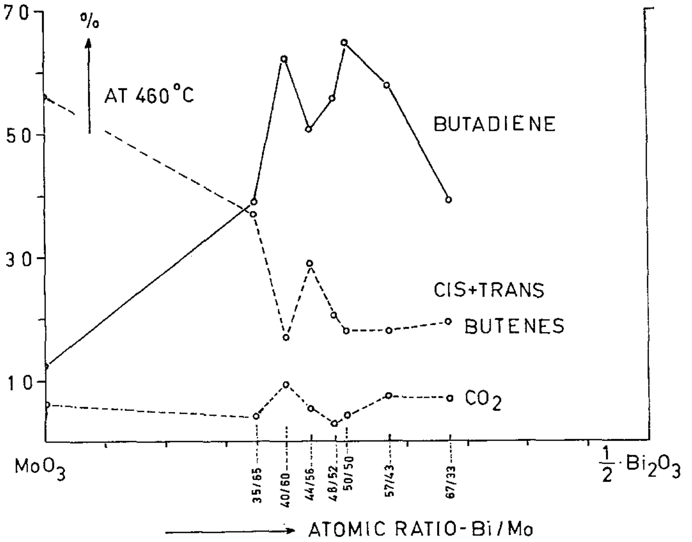


FIG. 4. Activity versus Bi/Mo compositions for oxidation of 1-butene to butadiene. Catalysts used are the C series at 460°C.

TABLE 3
SELECTIVITIES AT 460°C

Bi/Mo ratio	$S_1 = \frac{\text{Diene}}{100 - \text{(1)-butene}}$			$S_2 = \frac{\text{Diene}}{\text{Diene} + CO_2}$		$S_3 = \frac{\text{(2)-butenes}}{100 - \text{(1)-butene}}$	
	Diene	100-(1)-butene	S_1	Diene + CO_2	S_2	(2)-butenes	S_3
				B series			
80/20	7.0	12.4	56.4	10.3	68.0	2.1	16.9
67/33	16.0	19.1	83.7	17.3	92.5	1.8	9.4
62/38	35.3	46.1	76.6	36.6	96.4	9.5	20.6
57/43	42.4	53.2	79.7	43.7	97.0	9.5	17.8
53/47	53.6	62.3	86.0	55.0	97.5	7.3	11.7
50/50a	14.8	17.2	86.0	15.1	98.0	2.1	12.2
50/50b	26.3	30.0	87.6	26.9	97.8	3.1	10.3
48/52	57.7	70.6	81.7	58.6	98.4	12.0	17.0
46/54	41.4	51.2	80.8	42.3	97.9	8.9	17.4
44/56	38.7	44.8	86.4	39.6	97.7	5.2	11.6
43/57	34.0	40.9	83.1	34.7	98.0	6.2	15.2
40/60	5.9	6.8	86.8	6.2	95.2	0.6	8.8
37/63	6.1	9.4	64.9	6.1	—	3.3	35.1
35/65	12.8	21.6	59.2	13.0	98.5	8.7	40.3
MoO_3	2.5	12.1	20.7	4.6	54.3	7.6	62.8
				C series			
67/33	39.3	65.8	59.7	46.1	85.2	19.7	29.9
57/43	57.9	83.5	69.4	65.6	88.3	17.9	21.4
50/50	64.6	87.0	74.3	68.9	93.8	18.1	20.8
48/52	55.6	78.8	70.6	58.4	95.2	20.5	26.0
44/56	50.6	84.8	59.7	55.9	90.5	28.9	34.1
40/60	62.7	88.9	70.5	72.1	87.0	16.8	18.9
35/65	39.0	79.9	48.8	49.2	79.3	37.0	46.3
MoO_3	12.2	74.4	16.4	18.3	66.7	56.1	75.4

the conversion of 1-butene to butadiene at a temperature of 530°C.

The conversion to 2-butenes at a certain temperature appears to follow the general activity pattern if Bi/Mo > 1 but to increase considerably if the samples becomes rich in MoO_3 (Figs. 3 and 4). Finally, pretreatment at a lower temperature causes the 2-butene production to increase considerably. (Compare Figs. 3 and 4). This is particularly noticeable in the high-MoO_3 range. MoO_3 pretreated at 500°C is predominantly a double-bond isomerization catalyst with only a minor activity for oxidative dehydrogenation.

The *cis/trans* ratio of the 2-butenes formed is always observed to be very close to 1.

For one type of catalyst, sample B-46/54, i.e., an active catalyst in the B series, an attempt was made to determine the kinetics of the reaction. For this purpose runs were made at two temperatures (556°C and 580°C) with varying amounts of sample, i.e., different contact times. Figure 5 shows that a plot of log Y_i (Y_i being the amount of butenes still present in the exit gases) versus the catalyst weight gives a straight line through the origin. This also applies for log Y, Y being the amount of 1-butene left in the exit gases, which is not surprising since the amount of 2-butenes formed is only small at this elevated temperature. The conclusion from this experiment is that the kinetics are fairly well represented by a first-order dependency on the 1-butene partial pressure.

Accepting that this observation is also valid for other compositions and pretreatments and that hence the relationship log $100/Y_i = kt$ is generally applicable, one might in the usual manner try to derive frequency constants and activation energies from Arrhenius plots. This has been done by plotting log log $100/Y_i$ versus the reciprocal temperature and one might hope that in view of the constancy of the contact time t the relation $\log \log 100/Yi = \log kt = \log k_0t - E/RT$ will be valid. Straight lines are expected with a slope from which E is to be derived and with an intercept that is given by $\log k_0t$. Some of these plots are given in Fig. 6 and it is clear from this picture that the lines are strongly curved, being steeper at the lower than at the higher temperatures.

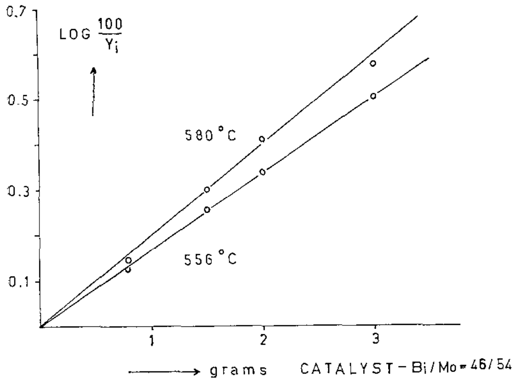


FIG. 5. First order plot of conversion of 1-butene to butadiene as a function of the amount of catalyst B-46/54 in reactor; Y_i, % butenes unconverted.

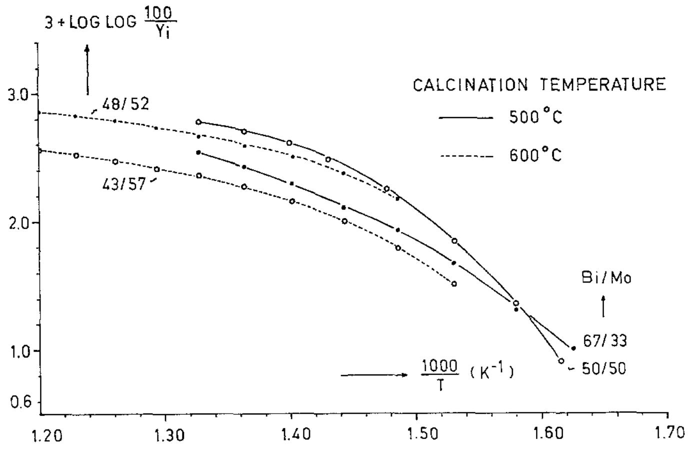


FIG. 6. Arrhenius plots of first order ratio constants versus the reciprocal temperature for reaction of 1-butene to butadiene. Numbers refer to catalysts as mentioned under "Preparation of Catalysts."

DISCUSSION

We shall first discuss the relations between activity and selectivity on the one hand and catalyst composition on the other hand, as given in Figs. 2, 3, and 4. "Activity" then is considered to concern the oxidative dehydrogenation. Since the selectivity is mainly determined by the degree in which the double-bond isomerization occurs we shall discuss this property in terms of "isomerization activity." Having dealt with the results in this way we shall then proceed with an attempt to fit them in a general reaction scheme.

Discussion of Results

The A series shows a pronounced activity peak in the region Bi/Mo = 0.4–2. Outside this region there exists almost no activity. The compounds identified by Bleyenberg *et al.*, in particular $Bi_2(MoO_4)_3$, and $(BiO)_2(MoO_4)$ are practically inactive. In the region 0.4–2 samples with a low activity are observed: The Bi/Mo = 1 composition is almost inactive. The "isomerization activity" is everywhere almost negligible, which is partly due to the high temperature at which the runs were performed.

The pattern of activity in the C series is similar to that observed in the A series: There are, however, a few important differences. The activity level is considerably higher and the region of active catalysts with respect to the Bi/Mo ratio is wider. The "lows" in the high activity have disappeared; the sample with Bi/Mo = 1 now shows a normal activity. The "isomerization activity" is surprisingly high even when taking into account the relatively low temperature at which the runs were performed. Its maximal activity does not coincide with that for the dehydrogenation reaction: It is almost completely situated on the Mo-rich side. Pure MoO_3 is primarily an active isomerization catalyst with only weak dehydrogenating properties.

The B-series samples are intermediate in catalytic properties between the A and the C series. The region of activity in dependency of the Bi/Mo ratio is considerably narrower than for the C but wider than for the A series. The most active samples in this region are almost as active as their C counterparts, but the "lows" begin to show up. The $Bi_2(MoO_4)_3$ sample is almost inactive, the $(BiO)_2(MoO_4)$ considerably less active than the C sample. The Bi/Mo = 1 samples show a variable behavior but they are generally low in activity. The isomerization reaction shows a similar pattern as in the C series, being concentrated mainly at the Mo-rich side. It is, however strongly inhibited and since the temperatures of the runs were identical to those for the C series the decrease in isomerization activity represents a significant observation.

One thing is clear from these observations: Dehydrogenation activity is not connected with the presence of one of the compounds in the Bi_2O_3–MoO_3 system. Maximal activity is concentrated around the Bi/Mo = 1 region. Isomerization activity seems especially concentrated in the Mo-rich samples.

This simple fundamental picture becomes complicated, however, by the occurrence of what we believe to be solid state reactions in the catalyst that begin to develop at temperatures higher than 500°C. A treatment at 600°C causes the activity of the samples in the range Bi/Mo = 0–0.4 to disappear almost completely, including that of the compound $Bi_2(MoO_4)_3$. The activities in the range Bi/Mo = $2-\infty$ are strongly diminished, including also that of $(BiO)_2(MoO_4)$. In the intermediate range 0.4–2 the decrease in activity is far smaller but the 50/50 ratio presents an exception since the loss of activity here is extensive. Parenthetically it may be remarked that our observations tally well with those of Adams *et al.* who report a loss in activity of their 1:1 catalyst if it is pretreated at temperatures above 500°C ("thermal collapse"). Moreover, the isomerization activity is generally much more reduced than the dehydrogenation activity.

What exactly happens during this collapse is not completely clear at this moment. It is certainly not a consequence of a change in crystallographic phase since the X-ray diagrams remain fundamentally the same before and after the 600°C pretreatment.

THE MECHANISM OF THE REACTION

Adams (*3*) postulates the following reaction mechanism:

$$O_2(\mathrm{gas}) \longrightarrow 2\,O_{\mathrm{ads}} \tag{1}$$

$$H_2C{=}CH{-}CH_2{-}CH_3 + O_{\mathrm{ads}} \longrightarrow H_2C\overset{\cdots}{-}CH\overset{\cdots}{-}CH{-}CH_3 + OH_{\mathrm{ads}} \tag{2}$$

$$H_2C\overset{\cdots}{-}CH\overset{\cdots}{-}CH{-}CH_3 + O_{\mathrm{ads}} \longrightarrow H_2C{=}CH{-}CH{=}CH_2 + OH_{\mathrm{ads}} \tag{3}$$

This scheme presents some unsatisfactory details. It stresses the intermediate formation of the allylic structure and with considerable justification, but it does not say how and where the allylic structure is attached to the surface. The formulation of the oxygen adsorption, moreover, leads us to expect a dependency of the rate on the oxygen pressure. Finally, it is not clear how water is dissociated from the surface. If we formulate this as

$$2OH_{\mathrm{ads}} \rightarrow O_{\mathrm{ads}} + H_2O \tag{4}$$

the set of reactions is complete.

Sachtler *et al.* introduce the reducibility of the catalyst as a determining parameter and consider the metal–oxygen bond strength as significant in this respect. Because they connect this parameter with an oxygen coverage (θ_0) one might perhaps formulate their proposal as follows:

$$O^{2-} \rightleftharpoons \tfrac{1}{2}O_2 + \square_r + 2e$$

where $\square_r$ is an anion vacancy obtained by reduction of the catalyst and e is an electron. If this reaction is supposed to be rate-determining the difficulties connected with the absence of an oxygen dependency in the kinetics of the reaction become particularly troublesome.

The dissociation of water now can be formulated in a somewhat more satisfactory manner, however,

$$2OH^- \rightarrow H_2O + \square_d + O^{2-} \qquad (4')$$

where $\square_d$ designates an anion vacancy obtained by dehydroxylation, i.e., without reduction of the sample.

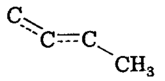
We now need to introduce a reaction that accounts for the double-bond isomerization. We choose to do this by reversing the allyl formation reaction. For instance,

$$C_4H_7 + OH^- + e \rightarrow \text{2-butene} + \square + O^{2-} \qquad (2')$$

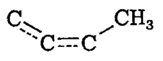
leaving for the moment undecided what type of vacancy we obtain by this reaction. Now the rate of this reaction is considerably faster on samples that have not undergone a heat pretreatment at 600°C. It seems attractive to introduce the concept that a fast rate of the reaction (2′) indicates a relatively large concentration of OH^- ions on the surface. In other words, the high-temperature pretreatment is equivalent to the dehydroxylation of the surface according to reaction (4′). The anion vacancy formed in (2′) is therefore similar to that formed in (4′) and is of the type $\square_d$.

Proceeding a step further we propose that the formation of the allyl structure occurs on an anion vacancy $\square_d$. It is hence *dehydroxylation, not reduction* that forms the anion vacancies necessary to adopt the allyl radical.

An interesting detail concerning the 2-butenes formed is that the *cis/trans* ratio is equal to 1, independent of catalyst sample or temperature. The conformer of the 2-butenes being the allylic structure we notice that this possesses a flat configuration and therefore can occur as the structures,



trans



cis

that are obviously the conformers of the *trans*- and *cis*-2-butene. The *cis* and *trans* allyl configurations therefore occur in a ratio equal to 1. However, their being equivalent rules out the possibility that the allyl is inserted perpendicular to the surface in the vacancy, the remaining possibility being an orientation parallel to the surface. This in its turn indicates that the allyl radical is π-bonded, which is only possible with a Mo ion because this possesses the necessary empty *d* orbitals. The molecular orbitals of the allylic structure are

$$\psi_{\mathrm{I}} = (1/\sqrt{2})\varphi_1 + \varphi_2 + (1/\sqrt{2})\varphi_3 \qquad \text{bonding}$$

$$\psi_{\mathrm{II}} = \varphi_1 - \varphi_3 \qquad \text{nonbonding}$$

$$\psi_{\mathrm{III}} = (1/\sqrt{2})\varphi_1 - \varphi_2 + (1/\sqrt{2})\varphi_3 \qquad \text{antibonding}$$

with φ_1, φ_2, φ_3, the $2p_z$ orbitals of carbon atoms 1, 2, and 3. The orbital ψ_{I} can interact with a metal e_g orbital to form a σ M.O. while ψ_{II} can interact with a t_{2g} orbital to form a π M.O. The position of the allylic plane is approximately perpendicular to the axis between the metal and the center of the allylic plane. There is room for four electrons in this $\sigma\pi$ double bond and one can therefore describe the adsorption complex as a hybrid between $C_4H_7^- \cdot Mo^{6+}$ and $C_4H_7 \cdot Mo^{5+}$.

Our conclusion from this consideration is that the allyl radical is bonded to Mo and that the relevant anion vacancy that adopts the allyl structure is connected with a Mo ion.

MoO_3 therefore should be a good dehydrogenation catalyst. That this is not the case is a consequence of the fact that the dehydroxylation reaction (4′) occurs only slowly, which is borne out by the fast isomerization. Bi_2O_3 may be supposed to dehydroxylate more readily but an anion vacancy on Bi_2O_3 cannot form a π bond with the allyl structure. Therefore it lies at hand to assume the reactive site for the dehydrogenation to be

$$\begin{matrix} O^{2-} & \square \\ Bi^{3+} & Mo^{6+} \end{matrix}$$

The number of these sites is easily seen to be maximal at the Bi/Mo ratio equal to 1, thus explaining the experimental observation that activity is maximal at this ratio.

Summarizing, our reaction scheme now is

$$2\mathrm{OH}^- \rightarrow \mathrm{H_2O} + \square_d + \mathrm{O}^{2-} \qquad \text{(a)}$$

$$\square_d + \mathrm{C_4H_8} + \mathrm{O}^{2-} \rightleftharpoons \mathrm{C_4H_7}^- + \mathrm{OH}^- \qquad \text{(b)}$$

$$\mathrm{C_4H_7}^- + \mathrm{O}^{2-} \rightarrow \mathrm{C_4H_6} + \square_r + \mathrm{OH}^- + 2e \qquad \text{(c)}$$

$$\square_r + \tfrac{1}{2}\mathrm{O_2} + 2e \rightarrow \mathrm{O}^{2-} \qquad \text{(d)}$$

where $\square_d$ is the anion vacancy on a Mo^{6+} ion that is neighbor to a Bi^{3+} ion and $\square_r$ is the same vacancy now, however, on a reduced metal-ion system. Since reduction has to occur anyhow, the arguments of Sachtler and de Boer in favor of reducibility as a determining parameter retain their validity. However, the oxidation reaction now occurs at a more convenient moment and cannot interfere with the reaction (b) that we consider rate-determining, in agreement with Adams.

The promotor action of Bi^{3+} for the dehydrogenation is seen to be located in two properties: (1) its role in facilitating the dehydroxylation, and (2) its reducibility. The inhibitory function of Bi for the isomerization and hence its favorable action as regards the selectivity is given by the first property.

Finally we shall summarize the thermal collapse phenomena as follows:

$$\square_d + \mathrm{O}^{2-} \rightarrow \text{sintering} \qquad \text{(e)}$$

We may therefore have to do with crystal growth phenomena that will manifest themselves primarily in a decrease of the surface area. However, observations such as the change in color from yellow to grayish that accompany this process might indicate a more profound change in the properties of the surface. Our present data are insufficient to express a definite opinion, mainly because the surface area determinations available are not accurate enough for this purpose. Experiments are now in progress to extend our knowledge here.

THE KINETICS OF THE REACTION

We have succeeded in eliminating the troublesome feature of the absence of an oxygen dependency in the kinetic expression for the rate but only at the cost of introducing another difficulty. It will be evident from our reaction scheme that the rate should be dependent on the water vapor pressure. So far only a dependence on the 1-butene partial pressure has been recorded.

However, we do not believe, judging from our preliminary observations, that the kinetics of the reaction have been examined in sufficient detail. It has been shown that the Arrhenius plot of the first order reaction constant shows a pronounced curvature, thus suggesting that at lower temperatures a different reaction begins to be rate-determining. This could, for instance, be the dehydroxylation reaction (a) which might be in agreement with the observation that at lower temperatures the isomerization reaction begins to be observable.

Other explanations are possible, however, to explain this phenomenon. A more detailed investigation into the kinetics is therefore indicated and experiments have been started in this direction that already showed the kinetics to be more involved than believed so far. We hope to report on this work in a future publication.

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REFERENCES

1. BLEYENBERG, A. C. A. M., LIPPENS, B. C., AND SCHUIT, G. C. A., *J. Catalysis* **4**, 581 (1965).

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

3. ADAMS, C. R., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* 1, 240 (1965).

4. MARGOLIS, L. YA., MALYAROVA, E. P., AND ROGINSKII, S. Z., *Izv. Akad. Nauk. SSSR Otdel. Khim. Nauk.*, p. 958 (1954).

5. MARGOLIS, L. YA., AND PLYSHEVSKAYA, E. G., *Izv. Akad. Nauk. SSSR Otdel. Khim. Nauk.*, p. 697 (1953).

6. SACHTLER, W. H. M., AND DE BOER, N. H., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* **1**, 252 (1965).