JOURNAL OF CATALYSIS **20**, 19–39 (1971)

Adsorption Equilibria and Rates of Reactions of Adsorbed Compounds on Reduced and Oxidized Bi–Mo Catalysts

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Received March 17, 1970

The adsorption equilibria of the butenes, butadiene and H_2O were determined on fully oxidized or partially reduced Bi–Mo catalysts as a function of the degree of reduction. The rate of reduction of the catalysts by butene and by butadiene and the rate of oxidation of reduced catalysts by O_2 were also studied in their dependence on the degree of reduction. The adsorption isotherms were found to follow simple Langmuir laws, either of the single or of the dual site type. This behavior was reflected in a linear or quadratic decrease or increase of the maximal volume adsorbable as a function of the degree of reduction. The adsorption of the hydrocarbons decreased with increasing reduction; that of water and oxygen proved to be zero on oxidized catalysts but to increase with increasing reduction.

Two types of adsorptive centers could be distinguished in this way, viz.,

(1) a single site that adsorbs butadiene in a slow but strong adsorption and that also acts as the adsorption site for H_2O and $\frac{1}{2}O_2$ in the reduced state (A center).

(2) a combination of three sites, two of which adsorb 1-butene, *cis*-2-butene but also butadiene in a fast but weak adsorption, the third one adsorbing *trans*-2 in a single site adsorption (B center).

The conversion of butene to butadiene was found to be a bifunctional process that involves the simultaneous cooperation of A and B centers. Combustion on the other hand starts from single A centers.

Reoxidation also proceeds from the vacant A centers provided the temperature does not exceed 400°C. Above this limit a new process sets in, the rate of which is not determined by a diffusional process but instead by a surface reaction. The nature of the latter process is still obscure. The heat of adsorption of H_2O on the reduced A centers was found to be so low as to provide an explanation for the absence of an inhibition by water in the conversion to butadiene.

INTRODUCTION

It is generally believed that the reaction mechanism of the oxidation of olefins such as propene and butene or of mixtures of propene and NH_3 over catalysts such as the Bi–Mo oxide combinations is reasonably well understood by the acceptance of an intermediate allyl structure (*1*, *2*). There are, however, a number of details in the mechanism that remain uncertain. To mention a few points on which opinions are still divided:

(a) How does O_2 enter into the reaction? Must it be adsorbed on the surface before reacting as advocated by Adams (*1*) or is the reaction essentially one between hydrocarbon and the O^{2-} ions of the oxide combination as proposed by Sachtler (*2*, *7*) and Batist *et al.* (*3*), a mechanism in which gaseous oxygen only serves to reoxidize the catalyst, previously reduced by the hydrocarbon? And if the latter assumption happens to be better suited to explain the ex-

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perimental data, does reoxidation occur on the same surface plane as the interaction with the hydrocarbon or do we need to assume a diffusion of O^{2-} from one surface plane to another by transport through the bulk of the catalyst, a possibility raised by Batist *et al.* (*4*) based on the observation that extensive diffusion can be demonstrated to occur under the circumstances at which the reaction proper takes place.

(b) If an allyl intermediate is essential for the reaction, how then is this intermediate bonded to the surface? Is it by a formation of σ-bonds to the surface O^2-ions (Sachtler *et al.*) or is it by π-bond formation to an exposed Mo^{6+} cation as postulated by Batist *et al.* (*3*)?

(c) Batist and Adams have independently come to the conclusion that the oxidation can be inhibited by the products of the reaction. Adams (*1*) mentions that the inhibition is especially strong for products such as acrolein while Batist and Prette (*5*) showed butadiene to inhibit the butene–butadiene reaction under steady-state conditions such as experiments with continuous flow or with recirculation. On the other hand, pulse experiments by Batist and Keizer (*6*) did not show an effect of butadiene in their kinetic expression for the rate as function of the partial pressures of reactants and products. One problem is therefore how to account for the discrepancies in the results performed with different techniques. Another is how to understand the inhibition of a compound such as butadiene in terms of the allyl intermediate.

(d) One product that is always formed and that can be assumed *a priori* to act as an inhibitor, H_2O, has never been found to inhibit the rate. Can we account for the absence of inhibition by steam?

The answers to these questions are difficult to give because of the absence of any information as to the adsorption equilibria of the various reactants and reaction products. It was therefore decided to investigate these equilibria in some detail.

A point of importance in this connection is how adsorption responds to previous reduction of the catalyst. As will be shown later, it was this part of the study that brought forward a number of interesting details not only of the adsorption processes proper but also of the mechanism of the catalytic reaction that was included in the study of the influence of the degree of reduction. The results of this investigation for the special case of the butene–butadiene conversion over Bi–Mo catalysts are reported in this paper. They will be discussed in particular with respect to their relevance in connection with the problems raised above. We believe that they are moreover of considerable importance in connection with the relationship between catalyst structure and the rate and selectivity of the oxidation. It is intended to publish these considerations in a further paper.

Experimental Procedure

All measurements were carried out in a conventional adsorption apparatus (Fig. 1), consisting of an adsorption vessel, a vacuum pump with MacLeod manometer for pressure readings and gas bulbs to introduce the material to be adsorbed on the catalyst. The adsorption was determined by measuring pressure changes in a system of constant volume and from the results adsorption-desorption isotherms were derived. One gram of catalyst was used unless otherwise stated.

The adsorption equilibria were measured over a wide range of pressures varying from 10^{-4} to 10 mm and in a range of temperatures between 25° and 450° for oxygen, between 0° and 80°C for butene, and between 25° and 250°C for butadiene. The procedure to start from a catalyst in a well defined oxidized state was as follows: the adsorption vessel, surrounded by a furnace, was heated at 450°C and pumped until a pressure $<10^{-5}$ mm was obtained. Then oxygen was admitted to the system to a pressure of 100 mm and the catalyst was heated at 450°C for one hr. Then the catalyst was cooled to the temperature for the adsorption experiment and the excess of oxygen was pumped off. After this treatment a known amount of gas was introduced to measure its adsorption.

Partially reduced catalysts were prepared by adding butene to the previously evacuated sample at a temperature of

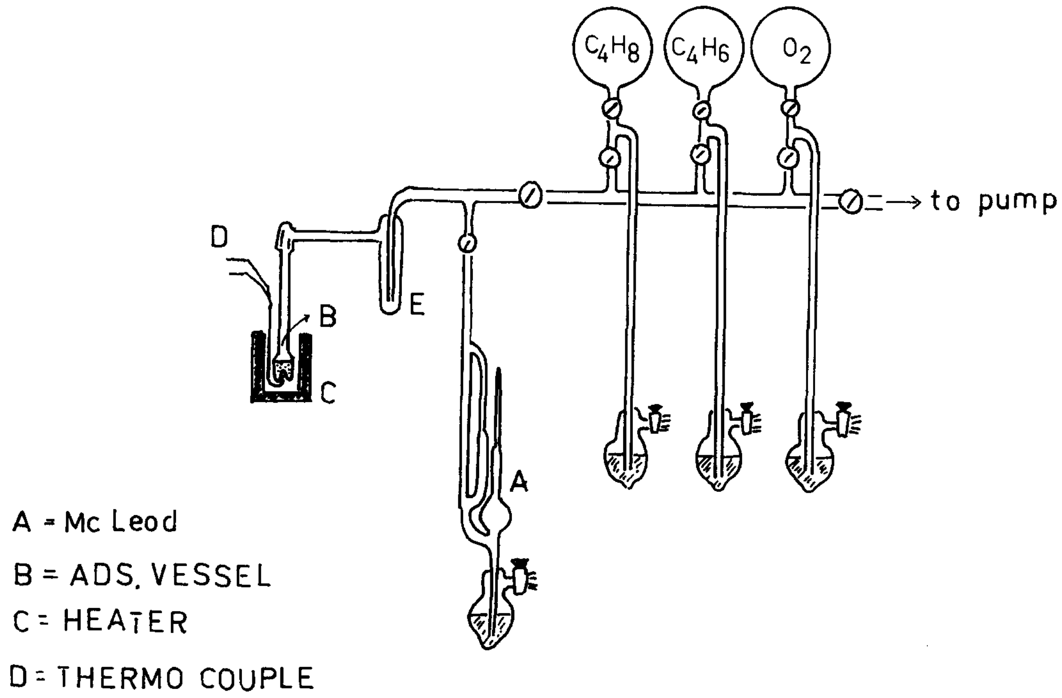

FIG. 1. Adsorption apparatus.

400°C. Reduction was assumed to occur according to the reaction:

$$C_4H_8 + O_{cat} \rightarrow C_4H_6 + H_2O$$

where O_{cat} is oxygen in the catalyst. Since care was taken to adjust the butene pressure in such a way that the final water vapor pressure always remained below the condensation point the degree of reduction could be ascertained from the rise in pressure. By varying the time of interaction, the degree of reduction could be fixed at the amount desired. Subsequent to this pretreatment, residual butene and the reaction products were pumped off at 400°C. To remove adsorbed material, the temperature was increased to 450°C under continuous pumping after which the sample was cooled to the temperature of the adsorption measurement.

Catalysts

The catalysts investigated were:

$2\ Bi_2O_3 \cdot MoO_3$ (Bi–Mo = 4/1)
$Bi_2O_3 \cdot MoO_3$ (Bi–Mo = 2/1)
Koechlinite modification
$Bi_2O_3 \cdot 2\ MoO_3$ (Bi–Mo = 1/1)
Ermann modification
$Bi_2O_3 \cdot 3\ MoO_3$ (Bi–Mo = 2/3)
MoO_3

For the preparation of the catalysts see Batist *et al.* (*4*). The properties of the samples applied here were similar to those described in their paper. All catalysts were preheated at a temperature of 500°C except the 1/1 sample which was heated at 600°C in order to prepare the Ermann modification. The surface area of MoO_3 was determined as 0.3 m^2/g.

Mathematical Expressions for the Adsorption Isotherms

All adsorption processes observed were found to obey one of the following expressions:

1. *Single-site Langmuir–Hinshelwood adsorption isotherm (SS)*

$$\frac{1}{V} = \frac{1}{V_m} + \frac{1}{V_m} \cdot \frac{p_0}{p} \tag{1}$$

2. *Dual-site Langmuir–Hinshelwood adsorption isotherm* (*DS*)

$$\frac{1}{V} = \frac{1}{V_m} + \frac{1}{V_m} \cdot \frac{p_0^{\frac{1}{2}}}{p^{\frac{1}{2}}} \qquad (2)$$

V_m being the volume maximally adsorbable at full coverage and V the volume actually adsorbed, both expressed in cm^3/g at STP. The final pressure obtained at the end of the adsorption, p, is given in mm as is the "pressure for half coverage," p_0. Finally,

$$p_0 = p_0{}^0 \exp\left(-Q/RT\right) \qquad (3)$$

where Q (kcal/mole) is supposed to represent the heat of adsorption.

EXPERIMENTAL RESULTS

Adsorption of 1-Butene

The adsorption equilibria were measured in the temperature range 0–80°C where the adsorption was found to be fast and reversible. The application of higher temperature was considered undesirable in view of the possible occurrence of double bond isomerization that was known from earlier experiments (Keizer and Batist) to start around 120°C, while physical adsorption might occur at lower temperature.

Measurements were also performed on partly reduced 2/1 samples where the degree of reduction is given by the fraction of O atoms removed by the previous reduction procedure. No such data could be produced for the 4/1, the 1/1 and the 2/3 samples because reduction hardly occurs for the 4/1 while the amounts adsorbed on the reduced 2/3 and 1/1 were so small as to escape determination. The results are given in Figs. 2 and 3 and in Table 1. Attention is drawn to the difference in results for the 4/1 and the other samples, the first showing a single site adsorption isotherm while for all the others a dual-site type was observed.

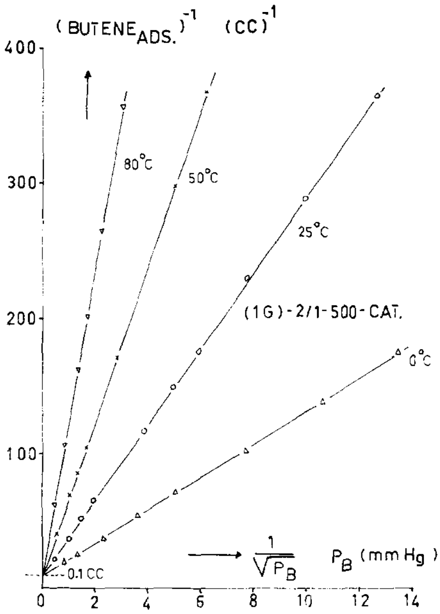

FIG. 2. Adsorption of 1-butene on a Bi_2O_3–MoO_3 catalyst dual site adsorption isotherm.

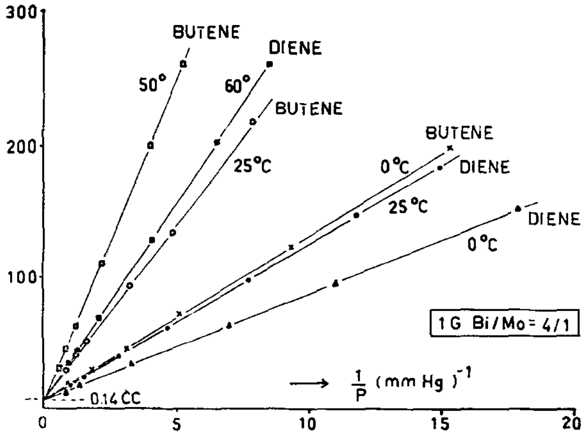

FIG. 3. Adsorption of 1-butene and butadiene on a $2Bi_2O_3 \cdot MoO_3$ catalyst; single site adsorption isotherms.

TABLE 1
PARAMETERS OF THE ADSORPTION OF 1-BUTENE

Catalyst	% O removed by reduction	Type of isotherm	V_m (cm^3/g)	log p_0^0 (mm)	Q (kcal/mole)
4/1	0	SS	0.14	3.99	4.8
2/1	0	DS	0.100	9.46	11.8
2/1	0.5	DS	0.090	9.52	12.0
2/1	1.0	DS	0.079	9.32	11.1
2/1	2	DS	0.058	9.36	11.7
2/1	3	DS	0.043	9.43	11.3
1/1	0	DS	0.061	9.12	11.8
2/3	0	DS	0.013	9.19	11.9
MoO_3	0	DS	0.033	9.31	12.0

Cis- and trans-2-Butene

Adsorption was only measured for the 2/1 nonreduced catalyst. The results were a dual-site adsorption type for *cis*-2-butene but a single-site adsorption for *trans*-2 with, however, equal maximal adsorption volumes (Figs. 4 and 5). The full results are given in Table 2.

Butadiene

The adsorption of butadiene at low temperatures on the 2/1 catalyst proved exceptional in that a fast and a slow process were found to occur. After some preliminary experiments it was found that the slow process showed the characteristics of a strong adsorption, i.e., necessitated much higher temperatures than the fast process to effect a desorption of the butadiene. This enabled the two processes to be investigated separately using the following technique.

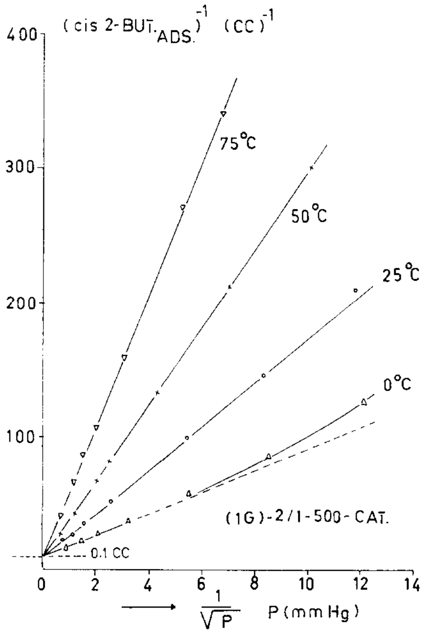

FIG. 4. Adsorption of *cis*-2-butene on a $Bi_2O_3 \cdot MoO_3$ catalyst; dual site adsorption isotherm.

Adsorption was measured for a relatively high pressure (5–7 mm) and at a low temperature (25°C), applied for 24 hr to attain equilibrium. The temperature was subsequently increased, first to 50°C and later to 100°C while at both temperatures the equilibrium pressures and adsorbed volumes were measured. At 100°C a known amount of gas was withdrawn from the system and the cycle of measurements was repeated. Proceeding in this way data were assembled as shown in Fig. 6. At temperatures below 200°C the amount adsorbed consists of two parts: a constant amount of 0.024 cm^3/g and a part that varies in quantity with the pressure. Subtracting the constant amount from the total adsorbed furnished the "weak and fast" adsorption.

TABLE 2
ADSORPTION OF *cis*- AND *trans*-2-BUTENE ON THE NONREDUCED 2/1 CATALYST

Hydrocarbon	Type	V_m (cm^3/g)	log p_0^0 (mm)	Q (kcal/mole)
cis-2	DS	0.10	8.32	10.8
trans-2	SS	0.10	6.67	9.9

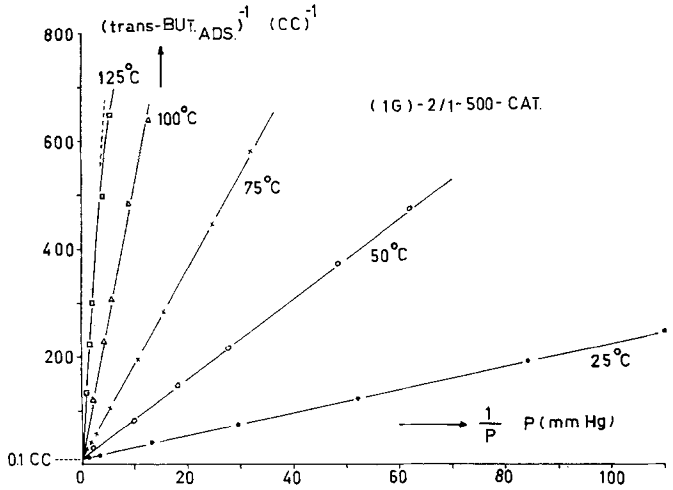

FIG. 5. Adsorption of *trans*-2-butene on the $Bi_2O_3 \cdot MoO_3$ catalyst; single site adsorption isotherm.

Experiments above 200°C, where the "constant" amount is seen to vary with the conditions, produced the characteristics of the "strong and slow" adsorption (Fig. 7). Further analysis of these data showed that the weak adsorption obeys a dual-site adsorption isotherm (Fig. 8) while the strong adsorption followed a single-site law (Fig. 9). Similar results were obtained for the partially reduced 2/1 catalyst.

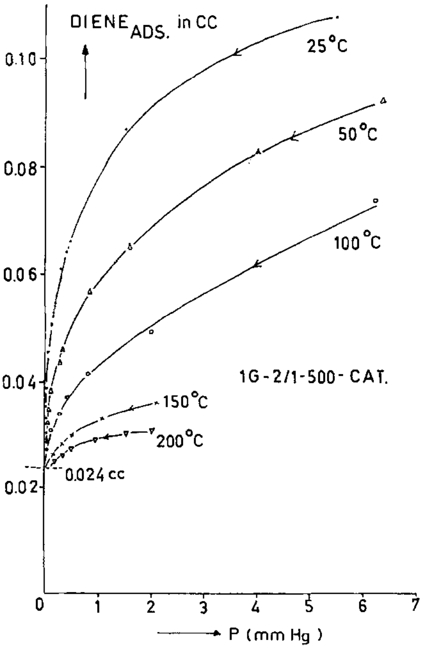

FIG. 6. The fast and "weak" adsorption of butadiene on $Bi_2O_3 \cdot MoO_3$.

As to the other catalyst samples, the 4/1 catalyst showed an entirely different type of single-site adsorption (Fig. 9). It proved impossible to separate weak and strong adsorption for the 1/1 and 2/3 samples while MoO_3 showed only a dual-site adsorption. The full results have been assembled in Table 3 except for the 1/1 and 2/3 samples because of the impossibility to satisfactorily analyze the data.

TABLE 3

ADSORPTION EQUILIBRIA OF BUTADIENE

Catalyst	% O red	Type	V_m (cm^3/g)	log p_0^0 (mm)	Q (kcal/mole^{-1})
			Strong adsorption		
2/1	0	SS	0.024	6.81	19.4
2/1	0.5	SS	0.024	6.79	18.6
2/1	1.0	SS	0.022	6.77	18.8
2/1	2.0	SS	0.019	6.87	18.9
2/1	3.0	SS	0.016	6.88	18.9
			Weak adsorption		
2/1	0	DS	0.112	6.62	9.2
2/1	0.5	DS	0.100	6.69	9.7
2/1	1.0	DS	0.085	6.64	9.6
2/1	2.0	DS	0.063	6.68	9.8
2/1	3.0	DS	0.049	6.72	9.4
MoO_3	0	DS	0.030	6.66	9.2
4/1	0	SS	0.14	3.87	5.0

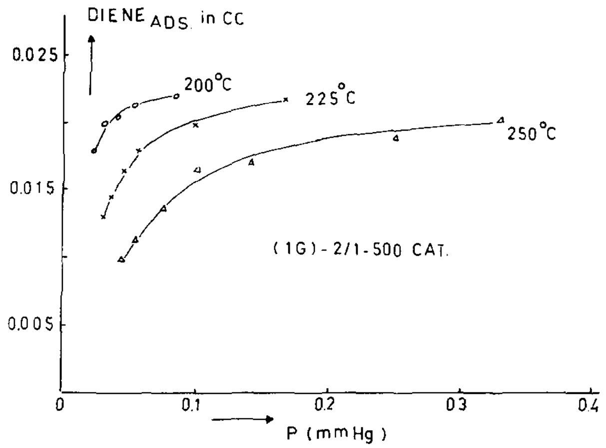

FIG. 7. The slow and "strong" adsorption of butadiene on $Bi_2O_3 \cdot MoO_3$.

Adsorption of H_2O

Adsorption of H_2O was measurable in the range 50–100°C provided the catalyst was reduced to some extent. To measure the adsorption, care was taken to maintain the water vapor pressures below 10^{-1} mm in order to prevent condensation. The adsorption equilibrium follows a single-site law as demonstrated in Fig. 10 for a 2/1 catalyst reduced for 3%. The parameters for the equilibria on various catalysts are given in Table 4.

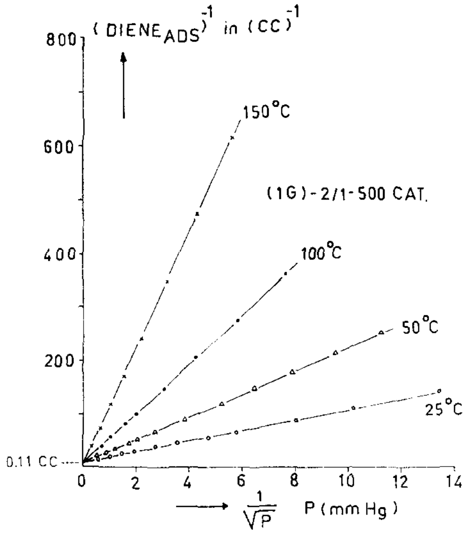

FIG. 8. Dual site isotherm for weak butadiene adsorption on $Bi_2O_3 \cdot MoO_3$.

TABLE 4
ADSORPTION EQUILIBRIA FOR H_2O

Catalyst	% O red	Type	V_m (cm^3/g)	$\log p_0{}^0$ (mm)	Q (kcal/mole)
2/1	0	—	—	—	—
2/1	0.5	—	—	—	—
2/1	1.0	—	—	—	—
2/1	2.0	SS	0.005	8.27	16.4
2/1	3.0	SS	0.008	8.25	16.2
1/1	0	—	—	—	—
1/1	0.67	—	—	—	—
2/3	0	—	—	—	—
2/3	0.75	SS	0.004	6.62	14.9

Sorption of Oxygen and Reoxidation of Reduced Catalyst

Nonreduced catalysts do not adsorb any oxygen; instead they dissociate a small amount at higher temperatures as shown in Fig. 11. The procedure to observe this (reversible) dissociation was to pump the sample at a certain temperature to a pressure $<10^{-5}$ mm and then to increase the temperature stepwise while measuring the pressure. It can be seen from the graph that the tendency to dissociate O_2 is greater for the 2/1 catalyst than for the 1/1 or 2/3 catalysts.

Adsorption sets in when a catalyst has been reduced beforehand and it increases the higher the degree of reduction. A qualitative picture of what happens if a reduced

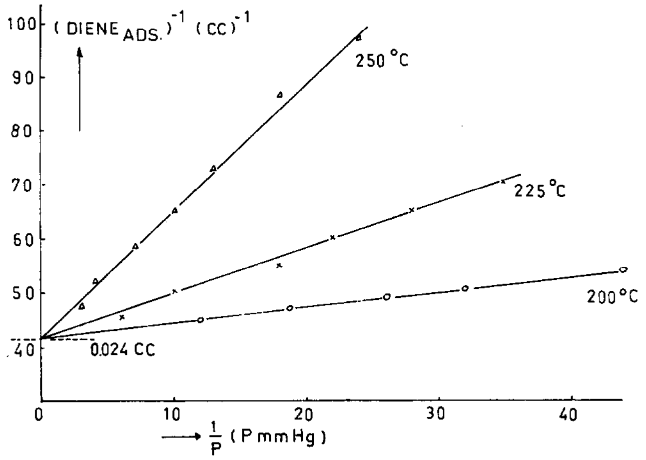

FIG. 9. Single site isotherm for strong butadiene adsorption on $Bi_2O_3 \cdot MoO_3$.

sample is brought into contact with an oxygen atmosphere at a pressure of around 1 mm while the temperature is increased at a constant rate (10°C/min) is given in Fig. 12. A small amount of O_2 is sorbed at room temperature in a very fast reaction but the sorption then stops. Increasing the temperature causes an increasing amount to be sorbed. Up to a certain temperature the amount sorbed is independent of the pressure but dependent on the degree of reduction. Once having passed this critical temperature, the position of which depends on the catalyst and its degree of reduction but which is generally situated between 300°C for strongly reduced catalysts and 400°C for slightly reduced catalysts, the sorption becomes dependent on the oxygen pressure. It therefore appears necessary to discuss the various sorption regions separately.

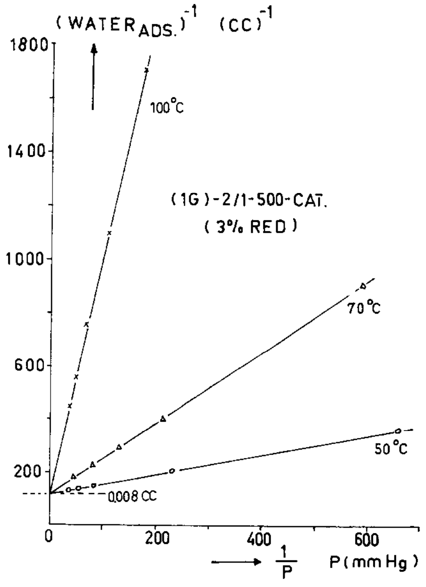

FIG. 10. Adsorption of H_2O on a partially (3%) reduced $Bi_2O_3 \cdot MoO_3$ catalyst; single site adsorption isotherm.

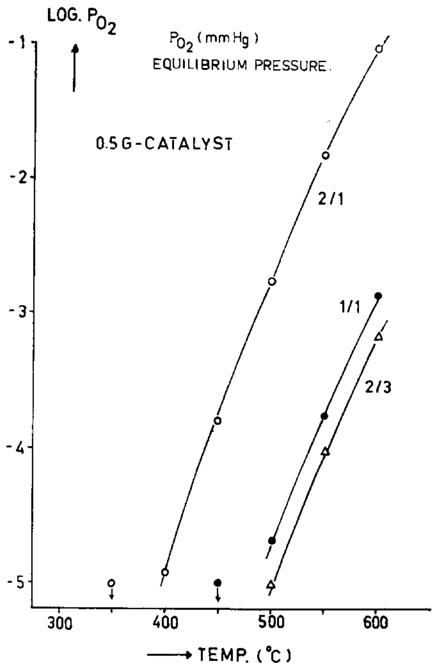

FIG. 11. Dissociation of O_2 from various fully oxidized Bi molybdates.

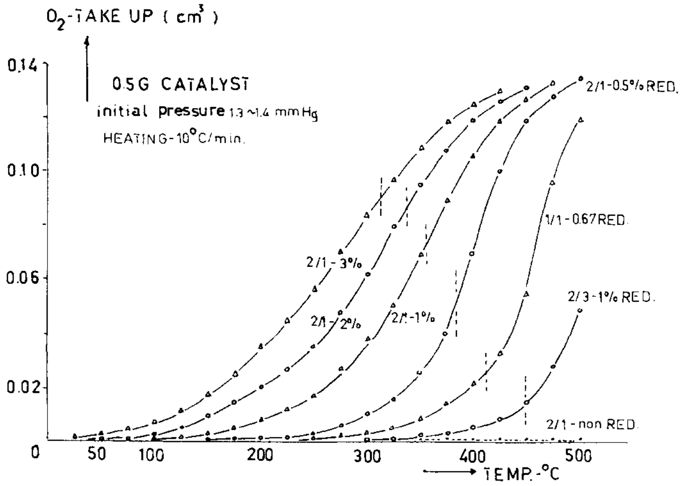

FIG. 12. Oxygen sorption of partially reduced $Bi_2O_3 \cdot MoO_3$ samples as a function of the degree of reduction.

The adsorption at room temperature. The adsorption is fast and all that can be measured is the amount adsorbed. The relevant data for various catalysts, reduced to different degrees, are given in Table 5.

For the sake of completeness it should be added that nonreduced MoO_3 shows a reversible adsorption with the following characteristics: single-site Langmuir isotherm, $V_m = 0.05$ cm³/g, $Q = 6$ kcal/mole. Reducing the catalyst to an extent of 1% eliminates this adsorption.

Sorption of O_2 between 20 and 400°C. Figure 13 demonstrates the manner in which O_2 is adsorbed on a reduced catalyst (2/1, 0.5% red) in the temperature range 300–400°C. It shows that the dependence of the sorption as function of the time is:

$$V_t = -C_1 + C_2 t^{\frac{1}{2}} \tag{4}$$

and that up to 380°C the rate is independent of the oxygen pressure.

TABLE 5

ADSORPTION OF O_2 ON REDUCED CATALYSTS AT ROOM TEMPERATURE

Catalyst	% O red	V (cm³/g)	at O ads/at O red $\times 10^4$
2/1	0	0	—
2/1	0.5	0.0004	3
2/1	1.0	0.0012	5.1
2/1	2.0	0.0024	5.1
2/1	3.0	0.0040	5.7
1/1	0	0	—
1/1	0.67	0.0004	2.1
2/3	0	0	—
2/3	0.75	0.0011	4.6

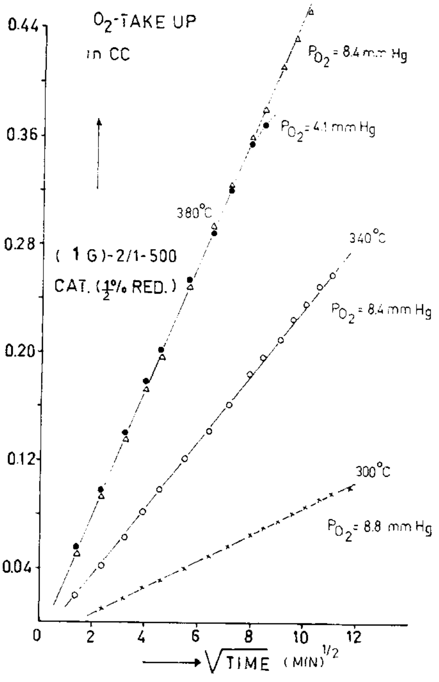

FIG. 13. Parabolic rate law (Eq. 4) for oxygen sorption in the range 300–400°C (Bi_2O_3–MoO_3).

A similar expression was derived by

Batist *et al.* (*4*) for the reduction of the catalyst by butene at temperatures higher than 400°C.

$$V_t/V_\sim = -A + Bt^{\frac{1}{2}} \qquad (5)$$

where

V_t = amount of gas consumed (sorbed) at time t (cm^3);
$V_\sim$ = maximal amount of gas reacted (sorbed) (cm^3);
$A = S\rho D/\alpha$;
$B = (2/\pi^{\frac{1}{2}})S\rho D^{\frac{1}{2}}$;
S = surface area (cm^2/g);
ρ = density of catalyst (g/cm^3);
D = coefficient of diffusion (cm^2/sec);
$\alpha = k\lambda$;
k = rate constant of surface reaction (sec^{-1});
λ = jump distance in solid (cm).

Since

$$D = D_0 \exp(-E_D/RT) \qquad (6)$$

we can rewrite Eq. (5) as

$$V_t = -AV_\sim + (B_0t)^{\frac{1}{2}} \exp(-E_D/2RT) \qquad (7)$$

with

$$B_0 = (4/\pi) \cdot S^2\rho^2V_\sim^2L_0 \text{ (cm}^6\text{/sec g}^2\text{)}. \qquad (8)$$

The data observed for various reduced catalysts with minute as time–unit are given in Table 6.

Since the coefficient of $t^{1/2}$ in Eq. (7) contains the surface area and because the accessible surface area could be diminished by adsorption of inhibiting substances such as H_2O that might block a surface vacancy or butadiene that might inhibit the O atom at the surface from moving inwards, an inspection of the dependency of the B factor on the presence of gases such as H_2O and butadiene appeared justified. In view of the temperature range, no inhibition by H_2O was expected but it was considered feasible that butadiene might show an inhibitory effect. Figure 14 shows that at 340°C there is no influence of H_2O while there is a marked inhibition by butadiene. The expression describing the influence of butadiene pressure on the oxygen sorption was found to be

$$\frac{1}{C_{2,p}} = \frac{1}{C_{2,0}} + ap, \qquad (9)$$

where $C_{2,p}$ and $C_{2,0}$ are the C_2 constants of Eq. (4) at a butadiene pressure of respectively p and zero, p being the pressure of butadiene in mm and a being a constant. The inhibition of butadiene is particularly evident at lower temperatures as seen from Fig. 15 and it disappears almost completely at 380°C.

TABLE 6
SORPTION OF O_2 BETWEEN 20 AND 400°C (EQ. 7)

Catalyst	% O red	log B_0 (cm^6/ min g^2)	E_D (kcal/ mole)
2/1	0.5	6.77	27.4
1/1	0.67	3.98	27.9
2/3	0.75	3.37	28.2
MoO_3	1.0	5.62	26.7

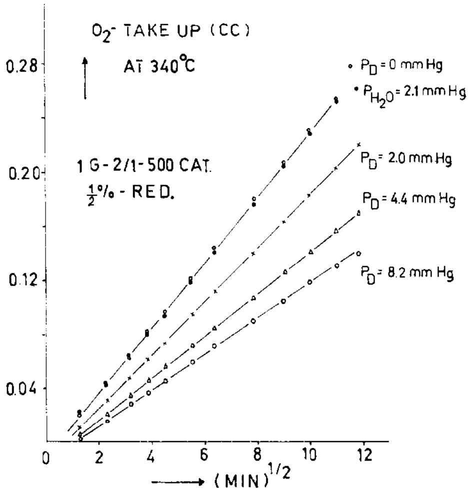

FIG. 14. Influence of water or butadiene on the rate of sorption of oxygen between 300–400°C on reduced $Bi_2O_3 \cdot MoO_3$ (Eq. 9).

Sorption of O_2 above 400°C. Figure 16 demonstrates the dependency of the rate of sorption on the pressure of oxygen at temperatures above 400°C, the catalyst sample being a 0.5% reduced 2/1 catalyst. It is clear from these data that the rate of sorption in first order in p_{O_2} and that the reaction can therefore be characterized by the first-order reaction constant k. It is further

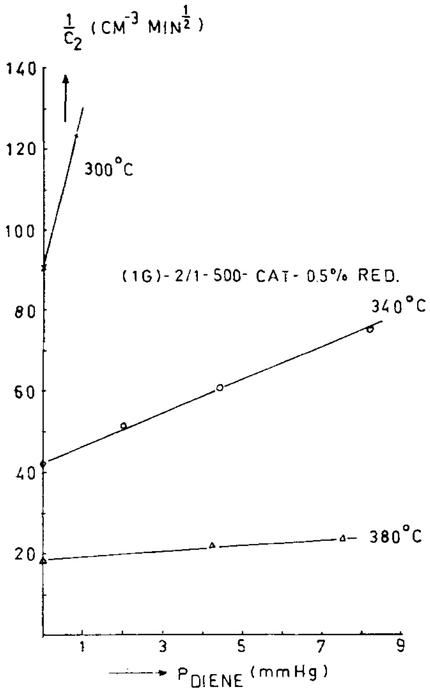

FIG. 15. Dependence of diffusion on the butadiene pressure according to Eq. 9.

shown in Fig. 17 that this rate constant is linearly related to the degree of reduction. To compare different catalysts, the Arrhenius parameters k_0 and E have been assembled in Table 7.

Reduction of the Catalysts by Unsaturated Hydrocarbons

Dehydrogenation of 1-butene on nonreduced and on reduced catalysts. The reactions were carried out in the same apparatus and very small amounts of butene gas ($<10^{-1}$ mm; $<10^{-2}$ cc) were brought to react with 1 g of the catalyst in the absence of gaseous oxygen; hence surface reduction reactions were actually investigated. The conversion of 1-butene as function of reaction time was determined from pressure changes according to the following reaction:

TABLE 7
FREQUENCY FACTORS AND ACTIVATION ENERGIES FOR THE SORPTION OF O_2 ON REDUCED CATALYSTS ABOVE 400°C

Catalyst	% O red	log k_0 (min^{-1})	E (kcal/mole)
2/1	0.5	4.83	16.9
1/1	0.67	6.57	22.3
2/3	0.75	6.64	23.6
MoO_3	1.0	6.37	23.0

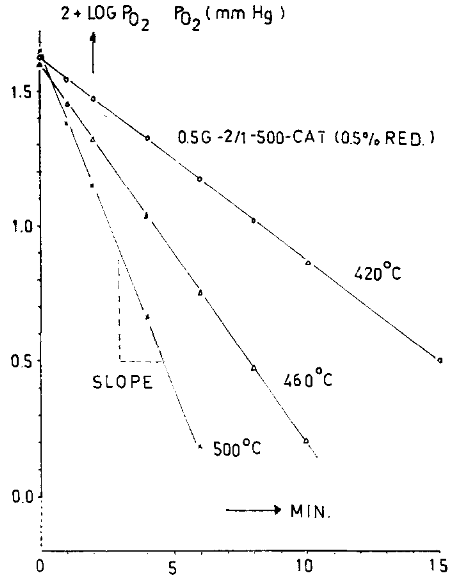

FIG. 16. Oxygen sorption above 400°C, influence of pressure: the equation followed is first order in the oxygen pressure ($Bi_2O_3 \cdot MoO_3$).

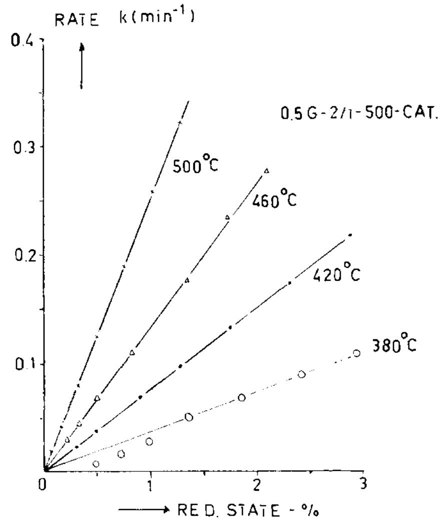

FIG. 17. The rate constant for the oxygen sorption of Fig. 16 in relation to the degree of reduction.

$$\underset{(1-\alpha)}{CH_3—CH_2—CH{=}CH_2} + Cat_{ox} \rightarrow Cat_{red} + \underset{(\alpha)}{CH_2{=}CH—CH{=}CH_2} + \underset{(\alpha)}{H_2O}$$

in which $1 + \alpha =$ total pressure measured and $1 - \alpha/1 + \alpha =$ butene pressure. Because of the low pressures ($<10^{-1}$ mm) water did not condense in the apparatus and because of the low reaction temperatures formation of carbon dioxide was small and negligible, so that our calculations are assumed reliable. In Fig. 18, the relation between the butene pressure and the reaction time is shown for a nonreduced 2/1 catalyst at various temperatures. The reaction is seen to be of the first order in the butene pressure and shows no inhibition if small amounts of butadiene (0.6 mm) or H_2O (0.5 mm) were present. Similar results were obtained for partially reduced catalysts and the experimental data, translated in the form of frequency factors and activation energies, are collected in Table 8.

TABLE 8
Rates of Dehydrogenation of 1-Butene

Catalyst	% O red	log k_0 (min^{-1})	E (kcal/ mole)
2/1	0	3.04	12.8
2/1	0.5	2.88	12.2
2/1	1.0	2.78	12.8
2/1	2.0	2.46	12.7
2/1	3.0	2.17	12.9
1/1	0	2.59	13.4
1/1	0.67	2.42	13.6
2/3	0	2.29	13.7
2/3	0.75	2.11	13.8

Dehydrogenation of *cis*- and *trans*-2-butenes on nonreduced 2/1 catalyst. For both 2-butenes, we have found the rate of the reaction in the absence of gaseous oxygen to be first order in the butene pressure. For the reaction with *cis*-2-butene we obtained an activation energy of 11.8 kcal $mole^{-1}$ and a log k_0 value of 2.87. For the reaction with *trans*-2-butene, we calculated an activation energy of 12.3 kcal $mole^{-1}$ and a log k_0 value of 2.84. These values are nearly equal to those obtained for the reaction with 1-butene.

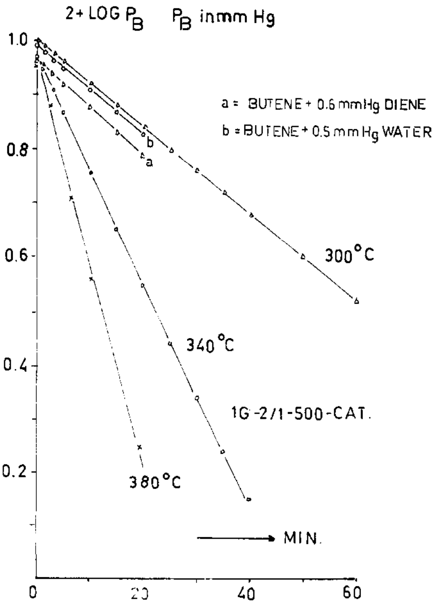

FIG. 18. Rate of the reduction of a $Bi_2O_3 \cdot MoO_3$ sample by 1-butene as a function of time: the rate is first-order in the butene pressure and no there is inhibition by small amounts of water and butadiene.

Combustion of butadiene to carbon dioxide. The reactions were carried out on 1 g of catalyst in the absence of gaseous oxygen between 300 and 500°C while the pressures used were very low (between 5.10^{-2} and 5.10^{-3} mm), so that actually surface reduction was measured. The conversion of butadiene as a function of time was determined from the pressure change according to following reaction:

$$\underset{1-\alpha}{CH_2{=}CH—CH{=}CH_2} + Cat_{ox} \rightarrow Cat_{red} + \underset{4\alpha}{4\,CO_2} + \underset{4\alpha}{4\,H_2O}.$$

In Fig. 19 the relation between butadiene pressure and reaction time is represented for a nonreduced 2/1 catalyst at different temperatures and from the straight lines a first order dependence on the butadiene pressure is derived. Furthermore it is shown in this figure that below 400°C butadiene hardly reacts. In Table 9 some data concerned with preexponential factors and activation energies are collected for various catalysts. It is shown that the activation energies for the Bi–Mo = 1/1 and 2/3 cata-

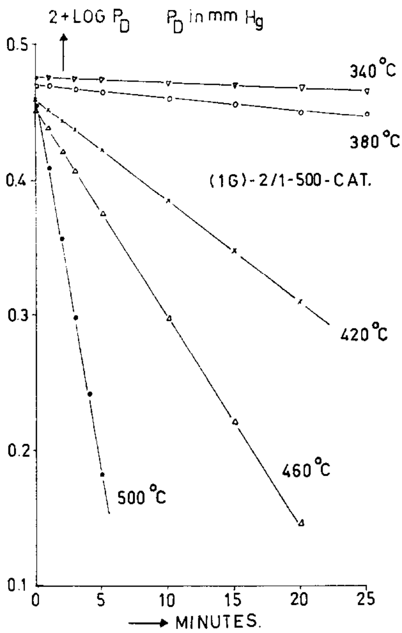

FIG. 19. Combustion of butadiene on a $Bi_2O_3 \cdot MoO_3$ catalyst as a function of time and temperature. Rate is first order in the butadiene pressure.

lysts are equal and those of the 2/1 catalyst are smaller.

DISCUSSION

The object of the discussion will be to systematize the experimental data in terms of (i) a few types of surface configurations, and (ii) of their concentrations as dependent on the state of reduction of the catalyst. In a later paper, we shall go a step further in an attempt to connect these configurations with the structure of the catalyst.

TABLE 9
COMBUSTION RATES OF BUTADIENE ON BI–MO CATALYSTS

Catalyst	% O red	log k_0 (min^{-1})	E (kcal/ $mole^{-1}$)
2/1	0	5.93	24.8
	0.5	5.89	25.1
	1.0	5.84	25.2
	2.0	5.80	25.4
	3.0	5.73	25.2
1/1	0	5.77	28.2
	0.67	5.73	28.7
2/3	0	5.50	28.1
	0.75	5.40	28.4

Since the situation at the surface of a reduced catalyst will be bound to enter into the discussion, it is necessary to mention what is known at the present moment about catalysts reduced by butene. It has been reported by Batist and Prette (*5*) that the particular 2/1 sample applied here cannot be reduced in excess of a limit that can be described by the formula $Bi_2MoO_{5.5}$ or in the scale used above 8.33% O red. It has not been investigated whether there exist similar limits for the other samples. If we confine our attention to this 2/1 catalyst for which the data are relatively abundant it becomes evident that they can be related to two different types of surface configurations.

Consider first the strong butadiene adsorption in its connection to the adsorption of H_2O and the room temperature adsorption of O_2 (Fig. 20). The strong diene adsorption appears to occur on one site judging from the adsorption isotherm. Its maximal adsorption volume decreases linearly from 0.024 cm³/g as the degree of reduction increases from 0 to 8.33%. On the other hand, the adsorption of H_2O, also a single site adsorption according to its adsorption isotherm, increases linearly with

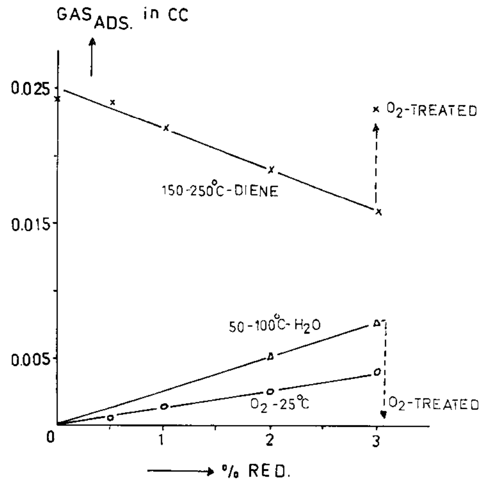

FIG. 20. Interrelation between maximal volumes for adsorption of butadiene (strong), oxygen and water as a function of the degree of reduction x (x_e = maximal reduction). Catalyst $Bi_2O_3 \cdot MoO_3$.

the degree of reduction from 0 to 0.024 cm^3/g if extrapolated to 8.33%. The room temperature adsorption of O_2 is zero at a fully oxidized catalyst. It increases to a value around 0.012 cm^3/g for a reduction of 8.33%. Moreover, the adsorption of butadiene that was decreased by a previous reduction, can be brought back to its original value by the room temperature adsorption of O_2. We can therefore propose with some confidence that the strong adsorption of butadiene occurs on a single surface O^{2-} and that the surface vacancy formed by its reduction is the site that adsorbs H_2O. Since one O_2 molecule should be able to fill two of these vacancies, the amount of O_2 adsorbed is equal to half that for butadiene or water. Moreover, these particular vacancies and therefore also the O^{2-} ions appear to occur in pairs since otherwise the adsorption of O_2 could not be as fast as observed. From now on, this type of site will be called an A center. The way in which butadiene can be attached to a single O^{2-} is given in Fig. 21 and it must therefore be related to one of the intermediate products, (furane), in the combustion of butene to CO_2 and CO. We shall return to this point later.

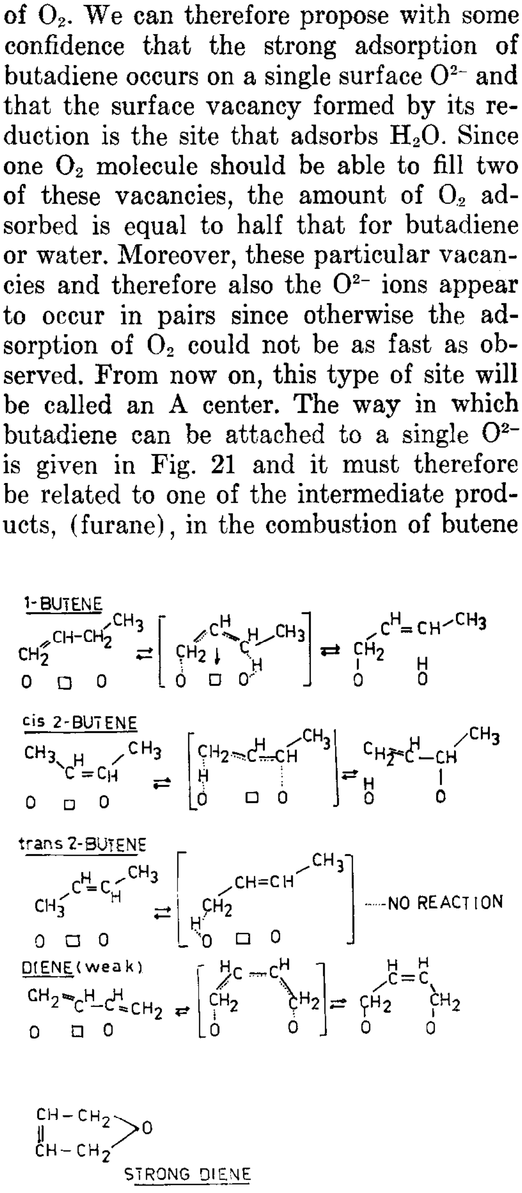

FIG. 21. Models for the adsorption of butene and for butadiene (weak and strong adsorption). Catalyst $Bi_2O_3 \cdot MoO_3$.

Since we have identified a special surface configuration on the 2/1 catalyst, let us see whether similar situations exist on the other catalysts, confining ourselves for the moment to those with higher Mo content. MoO_3 does not appear to possess any of the characteristic adsorptions so the site does not occur on its surface. However, once Bi is present both the adsorption of H_2O and the room temperature adsorption of O_2 appear to be present, provided the catalyst is reduced. The ratio of O(adsorbed) to O(reduced) is similar on all catalysts (see the last column in Table 5). So the concentration of A centers is comparable. However, it turns out to be impossible to separate strong and weak butadiene adsorption: if the site is present, its properties have been altered by the increase in Mo. This qualitative change is also shown by the parameters of the H_2O adsorption, the heat of adsorption appears to be smaller. To summarize, the presence of an A center appears to be connected with the presence of Bi but its properties vary with the amount of Mo present.

Before leaving the A center it may be well to point out that it is the only one for which adsorption and desorption of H_2O has been established. Moreover, it is only a weak adsorption and at the temperatures applied for the catalytic oxidation, desorption must be fast and complete. A second case of interrelated adsorption data is given by 1-butene, *cis*-2 butene and the weak adsorption of butadiene that all occur according to a dual site adsorption law and moreover show equal volumes of maximal adsorption. It can therefore be assumed that the surface configuration on which these adsorptions take place is the same for all three. Moreover, it must be a different center than the A center because strong and weak adsorption of butadiene have been observed to occur simultaneously. We shall name it the B center.

The volume of maximal adsorption, V_m, decreases in a marked manner with increasing reduction. In view of the dual-site character of the adsorption one might suppose that the B center consists of two sites that can be deactivated or removed separately by the reduction. Suppose that there exist N such sites and that each has z neighbors. The simultaneous activity of two neighboring sites will then occur for

$$V_m = Nz\,(1 - \theta)^2$$

Assume further that $\theta = x/x_e$, where x is the percentage reduction and $x_e = 8.33\%$. Then

$$V_{m,x} = V_{m,0}\left(1 - \frac{x}{x_e}\right) \text{ or,} \qquad V_{m,x}^{\frac{1}{2}} = V_{m,0}^{\frac{1}{2}}\left(1 - \frac{x}{x_e}\right) \tag{10}$$

where $V_{m,x}$ and $V_{m,0}$ are the maximal adsorption at respectively a % reduction of x and 0. It is shown in Fig. 22 that this relation is indeed well obeyed.

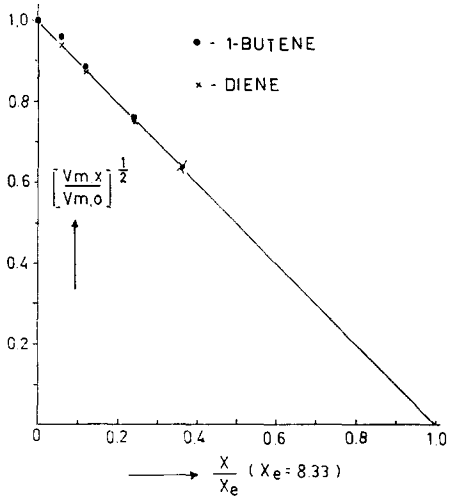

FIG. 22. Dependence of maximal volume of adsorption V_m for 1-butene and butadiene (weak) on the degree of adsorption according to Eq. 10.

trans-2-Butene adsorbs according to a single-site isotherm but its volume of maximal adsorption is equal to that of the other butenes. There must be a relation between the site on which the *trans* configuration is adsorbed and that producing the adsorption of the other butenes. Let us assume that 1-butene and *cis*-2-butene adsorb on two O^{2-} ions in accordance with the properties of the adsorption isotherm and the dependence on the degree of reduction. If we assume with Sachtler *et al.* (*7*) that the adsorption occurs via the formation of an allyl intermediate and a H atom, both bonded by σ bonds to the oxygen ions, we remain in agreement with current views. However, *trans*-2 must then be adsorbed by a different surface bond and we may suppose that this is the π bond advocated by Batist *et al.* (*3*). The particular *trans*-2 site is then a vacancy. We might now venture the following mechanism for the adsorption:

1. Olefin + $M^{n+} \rightarrow \pi$ complex
2. π complex + 2 $O^{2-} \rightarrow (OH)^- + (\text{Oallyl})^- + M^{(n-2)+}$

where M^{n+} is a metal ion.

The B center is then a combination of a vacancy and two O^{2-} ions which explains the stoichiometric relations between the volumes of maximal adsorption. *Cis*-2-butene and 1-butene perform reactions (1) and (2) in rapid succession while *trans*-2, perhaps due to steric hindrance, remains bonded via reaction 1. The weak adsorption of butadiene accordingly must also proceed via the formation of two σ bonds of its terminal carbon atoms to the oxygen ions concerned. These reactions have been shown in more detail in Fig. 21. Note that contrary to the assumption of Schuit (*9*), the σ bond formation is concerned with two different C atoms, viz. that dissociating the proton and another in β position that serves to attach the allyl. Moreover, if we assume that it is the reduction of the cation that stands in the way of the adsorption on reduced catalysts, the need to accept a *removal* of oxygen ions by reduction is eliminated. Since there exists no corroborating evidence for this removal in the form of oxygen or H_2O adsorption the present explanation offers a better fit to the experimental observations.

What happens to the B center if we pass from the 2/1 catalyst via the 1/1 and the 2/3 to pure MoO_3 is seen from Table 1. Its concentration decreases in a marked manner but its properties show little change. It is particularly interesting to find that it is still in existence on MoO_3. This observation reveals the nature of the cation concerned: it cannot be other than Mo and for M^{n+} we can further write Mo^{6+}.

The next question that should occupy us is what happens if, starting from the 2/1 catalyst, we proceed in the direction of higher Bi contents to the 4/1 catalyst. The change is quite dramatic since neither the A nor the B center are observed any more. Instead we find a new center, further to be called C center, that is quite different in its properties except for the fact that its maximal adsorption is approximately the same as that of the B center. The C center adsorbs both butene and butadiene according to a single-site mechanism but the heats of adsorption are much lower than those discussed so far. The change in surface characteristics, as revealed by the adsorption, is closely paralleled by that of the catalytic activity. As shown by Batist, the 4/1 catalyst has an inferior and remarkably different type of activity. Since we lack further information as to the nature of this center, it will not be discussed further.

We shall now pass on to a discussion of the reactions as observed in this investigation; the reactions of 1-butene and of butadiene with the catalyst. Butene has been found to react in a first-order process which is not inhibited by the presence of relatively small amounts of H_2O and butadiene and which is characterized by an activation energy of 12–13 kcal mole^{-1}. These properties are closely similar to those found by Batist and Keizer in pulse experiments concerning the oxidative dehydrogenation of butene to butadiene. To prove that the two reactions are indeed one and the same process, we have to prove that their rates are also comparable. Keizer operated with one gram of catalyst: assuming a density of the solid equal to 8 g/cm^3, a % void of 50 and a pressure of 2 atm, a contact time of 0.2 sec and a free volume around 0.1 cm^3. In our case, the contact time was of the order of 10^3 sec., the gas volume about 10^2 cm^3. The temperature range of the equal conversion being similar, we conclude that the rates are equal within a factor, 5, which appears satisfactory in view of the difficulties in comparing rates under pulse and static conditions. On the other hand, Batist and Prette for reactions in continuous flow and circulation showed the presence of a considerable inhibition by butadiene. From the data, collected for the strong and weak butadiene adsorption, see Fig. 23, it becomes possible to find the surface coverages at the pressures applied in the two cases. We calculate that in our experiments, the weak adsorption can be completely neglected while the strong adsorption could at best be 20%. The much higher pressures applied by Prette lead to complete coverage for the strong adsorption. The different sets of data are therefore not at variance but actually show a reasonable agreement.

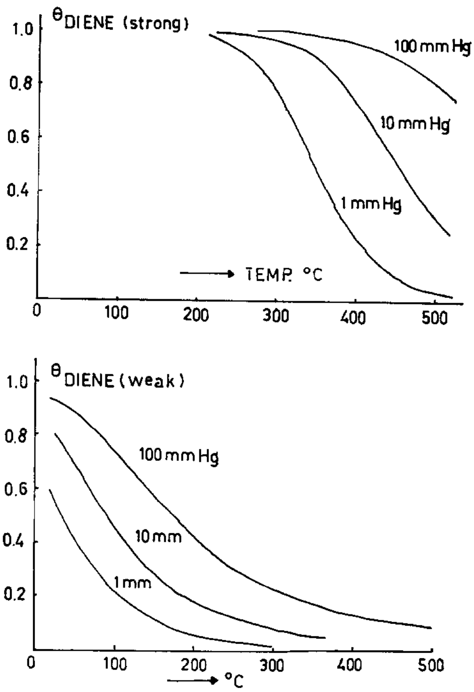

FIG. 23. Partial coverages for butadiene as a function of temperature extrapolated to higher temperatures: upper curves, strong adsorption; lower curves, weak adsorption.

Having established the identity of the reaction as observed here with the actual catalytic process, we shall proceed to investigate its rate as a function of the degree of reduction, by operating in a manner similar to that applied for the adsorption. The first-order rate constant k depends on the temperature according to

$$k = k_0 \exp(-E/RT).$$

Suppose that the reactive center contains p sites that can be removed or deactivated by the reduction. Then, if N is the concentration of the sites

$$k_0 = AN^p \text{ and}$$

$$k_{0,x} = k_{0,0}\left(1 - \frac{x}{x_e}\right)^p$$

which gives

$$\log \cdot \frac{k_{0,x}}{k_{0,0}} = p \log\left(1 - \frac{x}{x_e}\right). \qquad (11)$$

Plotting the data of Table 8 according to Eq. (11) leads to a value of p between 4.5 and 5. In Fig. 24 these data are given according to

$$\left|\frac{k_{0,x}}{k_{0,0}}\right|^{1/5} = 1 - x/x_e. \qquad (12)$$

We believe that the fit is reasonably good.

The problem now is, how to account for this remarkable dependence. As has been shown before, there exist two types of centers that can be brought into a relation with the actual reaction, (i) the B center that adsorbs the olefin, a necessary step in the reaction. It consists of three centers that are presumed to be deactivated by reduction. At least two of these may be involved in the reaction. (ii) the A center, that serves to furnish an O^{2-} ion for the acceptance of the two protons and from which the H_2O molecule can be desorbed. Its concentration is linearly related to the degree of reduction.

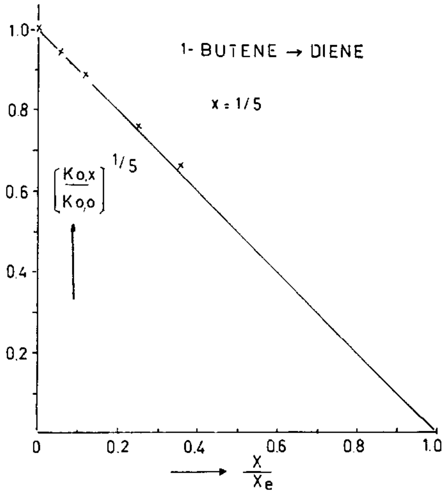

FIG. 24. Dependence of log k_0 for the reaction of butene with $Bi_2O_3 \cdot MoO_3$ on the degree of reduction x.

A combination of the two centers is able to account for the observed dependence according to the 1/5th power and is moreover logically required from the information obtained with reference to the adsorptive centers. In addition, there exists another observation than can be explained by the combination of the two centers. Butadiene is known to inhibit the catalytic reaction. The weak adsorption is too weak indeed to play a role in this connection as is shown in Fig. 22. It is the strong adsorption that has to be the inhibiting agent and since it occurs on the A center, this center is necessarily involved in the actual reaction system. Our final conclusion is therefore that the catalytically active center that we shall from now on call R center, is a combination of A and B centers. It is at the present time somewhat difficult to decide how many adsorption centers are combined in the reactive center. One A center and one B center, assuming the latter to contain three reducible sites, would add up to $p = 4$ but the experimental p appears nearer to 5. Various combinations might be constructed to fit $p = 5$ such as two B centers (each with two reducible sites hence without counting the vacancy) and one A center or one B center (with three sites) and two A centers. A point in favor of the latter combination is that the oxidation of propene cannot be imagined without assuming the cooperation of two A centers. At this moment we shall not make a choice in view of the scarcity of the data but shall restrict ourselves to the conclusion that the Bi–Mo catalyst is a bifunctional catalyst, the two functions being given by the A and B centers.

In view of the assumption that the B center is an essential part of the active R center, the strong decrease in its concentration, going from the 2/1 catalyst to the 2/3 catalyst should be reflected in a decrease in the activity. This is indeed found to be the case and from the few data available one forms the impression that this decrease is almost completely accounted for by the loss in B centers. That the A center is nevertheless a vital part is shown by the effect of its absence in pure MoO_3 which still contains a considerable amount of B centers; pure MoO_3 possesses only a slight activity for the catalytic process.

If we now pass to the combustion of butadiene to CO_2 etc. we encounter an entirely different picture. To recall the principle properties of this reaction: it only begins to become of some importance above 400°C and even then it is a slow reaction. It is of first order in the butadiene partial pressure and if the k_0 from the Ärrhenius equation is plotted vs the degree of reduction in the manner applied above (see Fig. 25) the number p is found to be near to *one*, a rather surprising finding in view of the fact that obviously quite a number of oxygen ions are needed to effect the combustion. It is tempting to identify this particular center with the O^2 ion in the A center and to assume further that the combustion is connected with furane like strong adsorption of butadiene. An explanation for the small number p could be that reduction by butene does not deactivate the remaining oxygen ions for the slow total combustion, or that the oxygen ions involved in this reaction form a different class that is not affected by the reduction. The information presently available does not allow a well-founded opinion on this point. An interesting detail is obtained by the comparison of the rates of the combustion on the 2/1, 1/1 and 2/3 catalyst. If indeed this reaction occurs on the A center, their concentration must be quite considerable on the samples that contain more Mo since the k_0 factors show only a decrease of a factor 3, i.e., far less than for the B center (Table 9). Their properties, however, do vary somewhat as shown by the increase of the activation energy that is in fact about equal to the decrease in the heat of adsorption of a water molecule.

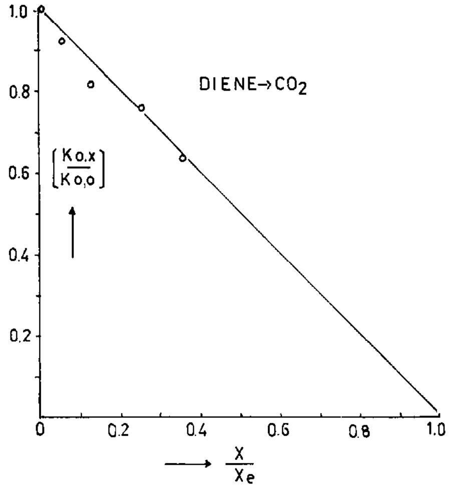

FIG. 25. Dependence of log k_0 for the reaction of the butadiene with $Bi_2O_3 \cdot MoO_3$ on the degree of reduction x.

The final point in the discussion will be concerned with the re-oxidation of a partially reduced catalyst. We have already identified *reduced A-center* as one site out of a pair that is able to bind O_2 at room temperature. It then has been shown that at temperatures below 400°C a process sets in that has all the characteristics of a bulk diffusion. Indeed, the activation energy of this diffusion process is around 28 kcal$\cdot$mole^{-1} and therefore equal to that obtained by Batist for the reduction of the catalyst. This, of course, has to be so since the properties of a diffusion must be independent of the way in which the concentration gradients are effected. The frequency factor connected with the coefficient of diffusion encountered here is also in satisfactory agreement with that calculated by Batist. To demonstrate this, we return to Eq. (8) and calculate D_0 from B_0, as given in Table 6. The surface area S of a normal catalyst is taken as 2 m^2/g or 2.10^4 cm^2/g. It has to be multiplied by a factor x/x_e because only a fraction of the surface is available in partially reduced catalysts. For ρ we assume the X-ray density given by *Zemann* (*9*) to be 8 g/cm^3. The maximal sorption for a fully reduced catalyst, i.e., Bi_2MoO_6–$Bi_2MoO_{5^1/_2}$ is 20 cm^3/g: it has to be multiplied by the factor x/x_e to produce the value for the partially reduced catalyst. Finally, multiplication factors for the conversion to seconds (1/60) and to one gram (=2) have to be included. We then find D_0 to be of the order 10^{-6} for the 2/1 catalyst, hence a factor 10^{-2} lower than that given by Batist. However, the surface area assumed here included the whole surface and from our assumption that only the A centers serve to adsorb the O_2 molecules, the actual surface area can be at most a factor 10^{-1} of the total area.

That indeed only A centers are active in taking up O_2 under the conditions assumed, i.e., below 400°C, is sustained by the observation that B_0 depends on the presence of butadiene and becomes smaller the more diene is present in the gas phase. The observation that this inhibition is still present above 300°C, where only the "strong" butadiene adsorption still exists (see Fig. 22), is convincing support for the assumption that the A center is the acceptor of O_2. Moreover, the dependence of C_2 in Eq. (4) as given in Eq. (9) shows that we have a one center adsorption of the butadiene. The constant C_2 in Eq. (4) is equal to αS, where α is a constant. If we assume that diffusion cannot occur as long as a surface oxygen ion is attached to a butadiene molecule, the effective surface area is

$$S = S_0 \cdot \frac{p_0}{p_0 + p}$$

and accordingly

$$C_{2,p} = C_{2,0} \cdot \frac{p_0}{p_0 + p}.$$

In other words:

$$\frac{1}{C_{2,p}} = \frac{1}{C_{2,0}} + \frac{1}{C_{2,0}p_0} \cdot p, \qquad (13)$$

an equation, similar to Eq. (9).

The model developed above appears completely self-consistent. However, it runs into two difficulties.

(1) It is in serious disagreement with the observation of Prette and Batist, who find the reoxidation to be very fast and independent of the presence of butadiene at 200°C. It is true that these measurements were obtained at a considerable higher O_2 pressure but in the temperature range concerned, this should have no influence since the surface reaction is assumed to be immeasurably fast, which it is already at room temperature. Accordingly, the rate of oxidation is solely concerned with the diffusion process, which is independent of the pressure. Moreover, the butadiene inhibition should be at its maximum here since the coverage is almost complete while the rate of adsorption should be fast.

(2) The experiments at temperatures above 400°C disclosed the presence of a sorption of O_2 that appears completely unrelated to that discussed so far. It is apparently connected to a surface process since it is first order in the pressure of oxygen. Moreover, it possesses a *high activation energy* that causes it to be negligible in rate at room temperature: it cannot therefore be connected with the adsorption observed at room temperature.

The combined evidence leads to the impression that there exists a second path in the reoxidation in which it is the rate of the surface adsorption that determines the overall velocity. It possesses a number of remarkable properties such as: (i) it is also present on MoO_3 contrary to the fast room temperature adsorption mentioned earlier, (ii) its rate depends on the first power of the number of vacancies in the reduced catalyst. Either the vacancies occur in pairs as in the case of the A centers, or the adsorption process has to be described in terms related to a surface specimen such as O_2^{2-} or a π bonded O_2 molecule; or (iii) from the fact that it is observable although it has to operate under a disadvantage because of its high activation energy, one has to conclude that there exist compensating factors for this disadvantage.

Either the number of surface sites involved in its operation are considerably greater than that of the process earlier discussed or the length of the diffusion path has to be considerably shorter, or both factors occur together. The impression is then gained of a catalyst structure made up of platelets with the actual catalytic reaction and the first oxidation originating on the edges while the second type of reoxidation is connected with the surface planes bordering the platelets at the top and/or the bottom (Fig. 26). Obviously, such a model is

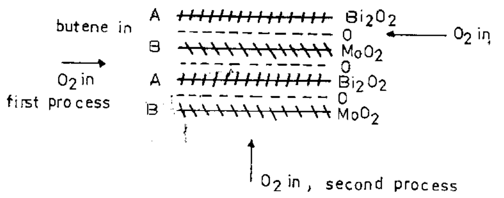

FIG. 26. Simplified model for the reduction and reoxidation of $Bi_2O_3 \cdot MoO_3$.

inherently connected with a steady-state reaction in which the oxygen enters the system at a different surface plane than that on which the reaction is occurring and it is therefore equivalent to the Batist model in which diffusion has to precede reaction. At this moment, it appears as if this model is inherently acceptable under certain special conditions such as high temperature, but it is certainly not the only one operative. A well-founded opinion on its importance will only be possible if we succeed in acquiring more information on the surface site that is involved in the acceptance of the oxygen, a site that we will name for sake of convenience an O center. To conclude this discussion let us summarize the outcome of this investigation. Adsorption measurements led to the acceptance of two different sites for the interaction with olefins and diene viz.,

(1) A three center site that interacts with the olefins but does not lead to oxidative dehydrogenation, although it may form allyl radicals (B center). Adsorption of olefins can occur in two ways i.e., by a dual site mechanism similar to a situation involving σ bonded allyl intermediates or by a single site adsorption that may involve π bonded intermediates. It has been postulated here that the second type precedes the first.

(2) A single site consisting of an O^{2-} ion in a special position that can interact with butadiene in a process that leads to an inhibition of the actual conversion but may also be the nucleus from which combustion starts (A center). If the oxygen is removed by previous reduction, the site acts as a nucleus for reoxidation of the catalyst. It is also the site from which a water molecule formed by the reaction leaves the catalyst.

The actual catalytic site is a combination of the two and the Bi–Mo catalyst is hence a *bifunctional catalyst.* This assumption explains some, hitherto enigmatic, observations. Adams (*1*) has observed that one of the strongest supports for the allyl intermediate consisted in the relative activities of the various olefins that followed the rules for the relative ease of H dissociation in olefins. On the other hand, inorganic evidence appears to support the relative ease of O dissociation as the determining factor. In the bifunctional situation, both factors have to be present simultaneously.

Oxygen adsorption is shown here to be connected with a reduced catalyst. There is abundant evidence to show that one of the entrance sites is the reduced A center. However, a second entrance appears to exist. The nature of this entrance is still somewhat obscure but it may lead to a reaction mechanism in which the oxygen enters the catalyst at a surface plane other than that from which it was removed by the reduction.

ACKNOWLEDGMENTS

I. Matsuura gratefully acknowledges financial support from the Kansai University and from the Organisation of Pure Research of the Netherlands (ZWO) that enabled him to perform this study.

Thanks are due to Ph.A. Batist for his constant help and interest.

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