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Adsorption and Reaction of Adsorbed Species on Bi_2MoO_6 Catalyst

Influence on Sintering and of Temperature of Reduction

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The adsorption of butene (B-sites), the strong adsorption of butadiene (A-sites) and the sorption of O_2 were studied on (partly) reduced and sintered samples of Bi_2MoO_6, in connection with studies on the rate of reduction of the catalyst by butene and the rate of reoxidation of reduced samples. The A-site concentration (A) was found to be independent of the surface area of the catalyst and to decrease linearly with the degree of reduction. The B-site concentration (B) falls to half its original value if samples are preheated to 600°C. B-sites remain present if the catalyst is reduced below 400°C but disappear if the reduction is performed above 400°C or when a reduced sample is heated above 400°C under vacuum. O_2-sorption is fast on samples reduced below 400°C but considerably slower on samples preheated above 400°C. For the latter samples a new, weak, molecular type of O_2 adsorption was observed. The rate of reduction is dependent on $(A)\cdot(B)^2$. A mechanism for the catalytic oxidation of butene to butadiene was proposed in which butene is first adsorbed on a B-site by σ-allyl adsorption, the allyl then moving over to an A-site and donating its second H-atom to another B-site. Reoxidation of a reduced sample starts at the A-site but at higher temperatures of reduction an internal rearrangement in the catalyst leads to a transfer of O^{2-} from MoO_2 layers to Bi_2O_2 layers, the A-sites being on the edges of the Bi_2O_2 layers.

INTRODUCTION

In a previous paper (*1*) we reported on the adsorption of butenes, butadiene, oxygen, and water on fully oxidized or partly reduced bismuth molybdates. This work led to the assumption of two different types of adsorption sites, viz. (a) A-sites that adsorb butadiene in a slow reversible process according to a single site Langmuir isotherm with a heat of adsorption of 19 kcal mol^{-1} ("strong" adsorption). The site is a surface oxygen anion (O_A): its surface concentration is low ($\sim 10^{17}$ m^{-2}). If removed by previous reduction H_2O can adsorb on the residual vacancy. O_2 is already adsorbed at room temperature on pairs of A-vacancies in a fast irreversible process. (b) B-sites, being clusters of two sites, presumably also surface oxygen anions (O_B). They adsorb butene and also butadiene according to a dual site Langmuir isotherm ("weak adsorption"). The heats of adsorption are 10–12 kcal mol^{-1}, and the surface concentration of the sites is a factor of 10 higher than that of the A-sites. Reduction of the binary oxide, in all probability equivalent to the catalytic oxidation, occurs on a cluster of O_A and O_B, the exact composition of which remained somewhat uncertain. We concluded provisionally that the cluster contained five oxygen anions of which at least one was an O_A and the others O_B. This cluster was named the R-site. The measurements also produced information on the mechanism of the reoxidation of a prereduced Bi_2MoO_6 (koechlinite) catalyst. Two processes were encountered, viz. (a) one operative at relatively low temperatures (200–400)°C with a rate independent of the oxygen pressure and inhibited by butadiene, but with kinetics which indicated bulk diffusion to be the rate determining process; (b) another only observable above 400°C, being first order on the oxygen pressure and the degree of reduction.

These results were explained on the basis of a model for the crystal structure of koechlinite proposed by Zemann (*2*) and earlier applied by Batist *et al.* (*3*) to explain the selectivity of Bi-molybdates for the catalytic oxidation of olefins. The crystals are assumed to be platelike (see Schaller (*4*)) and to consist of layers of $(MoO_2)_n^{2+}$ and $(Bi_2O_2)_n^{2+}$ interconnected by O_n^{2-} layers, the layers being parallel to the top and bottom faces of a crystal. The edges of the crystal were supposed to possess both O_A and O_B (and therefore also the reactive R-site) while the top and bottom faces were assumed to show only O_B. The low temperature, diffusion-controlled reoxidation was assumed to start from O_A, i.e., on the edges, and to proceed parallel to the layers. The high temperature process was connected with a surface reaction at the top and bottom planes and assumed to proceed perpendicularly to the direction of the layers. There is fairly good agreement between the kinetic measurements for the olefin oxidation of Batist *et al.* (*5*, *6*) and our adsorption results. However, there remained a discrepancy between the observations regarding the reoxidation since a process was encountered (*6*) that was already very fast at 200°C and moreover was uninhibited by butadiene. Careful checking of the reaction conditions disclosed a possible origin of the discrepancy. While Batist and Prette (*6*) reduced their catalyst during a short time at 430°C and then immediately cooled to lower temperatures to reoxidize the sample, we employed much longer times for reduction at higher temperatures, evacuated the sample for 3 hr at the higher temperatures (to remove hydrocarbon (HC) residue) and only then cooled to lower temperatures. It was therefore decided to reinvestigate the reoxidation in more detail applying also Batist and Prette's conditions. This led to some unexpected and interesting results.

Another aspect that merits further consideration is a more precise definition of the surface in terms of the bulk structure and the form of the crystals. A possible method to change the surface structure while maintaining the bulk structure is to sinter the solid under moderately severe conditions. According to former measurements in this laboratory (*3*) the koechlinite phase remains unaltered unless heated at temperatures above 600°C. In that work, however, it was also observed that reflection spectroscopy in the visible and uv showed a change presumably limited to the surface. This change is already observable with the naked eye because the catalyst loses its strong yellow color to become yellowish white. X-ray analysis of samples preheated for various periods below 600°C always showed the koechlinite pattern but with abnormal intensity ratios for samples preheated for only a short time. It was therefore decided to study the adsorption as a function of sintering time and temperature.

EXPERIMENTAL RESULTS

The majority of the measurements reported here are concerned with the adsorption of butenes and butadiene on samples of reduced or sintered Bi_2MoO_6, using the technique reported earlier (*1*). The preparation of the samples has been described by Batist *et al.* (*3*). Rates of reaction of butene with the solid catalyst and of O_2 with the reduced catalyst were measured in the adsorption apparatus as described earlier. The decrease of the surface area of the samples as a consequence of a high temperature treatment was also measured in this apparatus with N_2 as the gas adsorbed ("single point" method). To describe the results of the adsorption and reactivity measurements on reduced catalysts it will occasionally be necessary to connect a certain quantity such as a maximal volume of adsorption or a "frequency constant" with the degree of reduction x/x_e, where x_e is the maximal reduction (8.33% at 0). Frequency constants are then derived from the Arrhenius expression $k = k_0 \exp(-E/RT)$ without correcting for the number of sites involved in the reaction. The dependency on the degree of reduction is invariably of the form:

$$A_x = A_0(1 - x/x_e)^n \qquad (1)$$

where A is some quantity measured on a sample reduced to the degree x and n is a constant. In the following we shall only mention the quantity and the magnitude of n.

1. *Properties of Reduced Catalysts*

Catalyst samples were reduced by butene at some temperature and subsequently evacuated at the same temperature, but sometimes higher evacuation temperatures were used. After this pretreatment they were investigated as to their adsorption properties for butene and butadiene. Their reactivity in reduction by butene and oxidation by oxygen ($P \sim 100$ mm Hg, i.e., considerably higher than in the older experiments) was then measured.

a. Reoxidation of previously reduced samples. The parameters varied were the temperature at which the reduction was performed and the temperature of subsequent heating under vacuum. All samples investigated here were fully reduced. Figure 1 shows that the maximum temperature at which the catalyst has been exposed during its reduction determines its tendency for reoxidation: the higher this temperature, the higher the temperature at which reoxidation sets in. It is immaterial whether this temperature occurred during the reduction or the evacuation: A catalyst reduced at 350°C and subsequently evacuated at 500°C is similar in its oxidation properties to one reduced and evacuated at 500°C. A catalyst sample reduced in Batist and Prette's apparatus (*6*), cooled down quickly without any pumping and then transferred to our apparatus proved very reactive and very similar in properties to those described by them, thus showing that the differences between the results of Batist and Prette and our earlier measurements were entirely due to the pretreatment given to the catalyst. It is noteworthy that the latter catalyst sample still contained considerable quantities of hydrocarbon residues apparently without harming its reoxidation properties. It was observed during these experiments that at the higher oxygen pressures applied some of our samples showed an adsorption of O_2 around room temperature that considerably exceeded the small amount of irreversibly adsorbed O_2 reported earlier. This type of adsorption becomes observable only on samples reduced at a temperature exceeding 400°C (Fig. 2). It is a reversible and weak adsorption that fits a single site Langmuir isotherm and therefore is presumably a weakly adsorbed form of molecular O_2. The parameters of the adsorption for a sample reduced at 500°C are: $Q = 8$ kcal mol^{-1}; log $p_0{}^0 = 6.7$ ($p_0{}^0$ in mm Hg). For the symbols see Eq. (3) of our previous paper (*1*). The maximum volume was around 0.2 cm^3 g^{-1}, i.e., approximately double that of the butene adsorption on a fully oxidized sample.

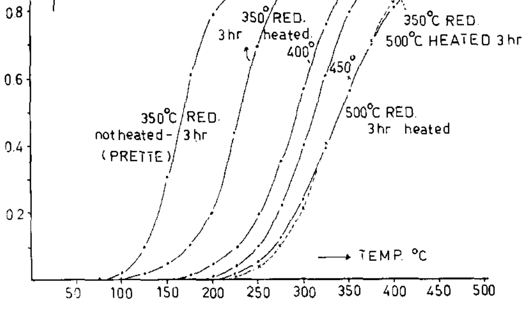


FIG. 1. Reoxidation of reduced catalysts as a function of the reduction temperature. Conditions: one gram Bi/Mo = 211 catalyst; initial pressure 100–200 mm Hg_{O_2}; heating speed 10°C/min.

b. Adsorption of butene and butadiene on reduced samples. The parameters of the adsorption processes are completely similar to those reported before and we can therefore restrict the discussion to the amounts adsorbed as a function of the temperature of reduction and the degree of reduction (Fig. 3). A sample reduced at 350°C showed only an impaired adsorption of butadiene, the maximum volume of adsorption decreasing according to Eq. (1) with $n = 1$. The numbers of O_A therefore decrease linearly with increasing reduction.

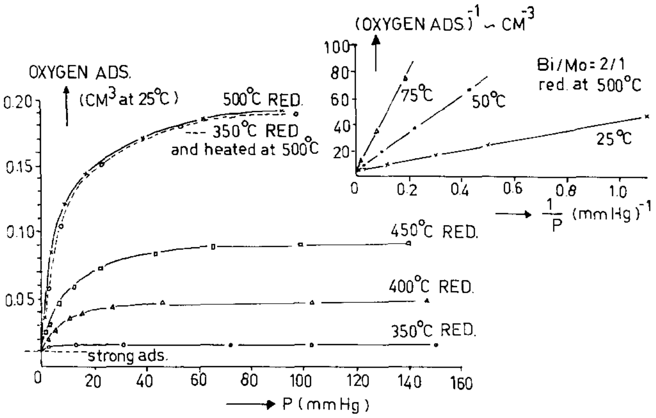


FIG. 2. Adsorption isotherms of oxygen on reduced catalysts at low temperatures.

If the reduction temperature exceeds 400°C also, the adsorption of butene diminishes according to Eq. (1) with $n = 2$. Under these conditions also the B-sites are eliminated. These results fully corroborate our earlier findings but there is one important additional piece of information, namely that O_A disappears at a lower temperature than the B-sites.

c. Rate of reduction of the solid as a function of the degree of reduction. The kinetic parameters of the reduction were similar to those determined earlier, i.e., first order in the partial pressure of butene and $E = 12$ kcal mol^{-1}. Plotting k_0 vs. the degree of reduction (Fig. 4) furnishes new information. For catalysts reduced at 350°C (that have partly or completely lost their O_A sites) k_0 decreases linearly with the reduction (n in Eq. (1) being equal to 1). If reduced at temperatures above 400°C (where also the B-sites become eliminated) the fall with the degree of reduction is more pronounced, n now being 5.

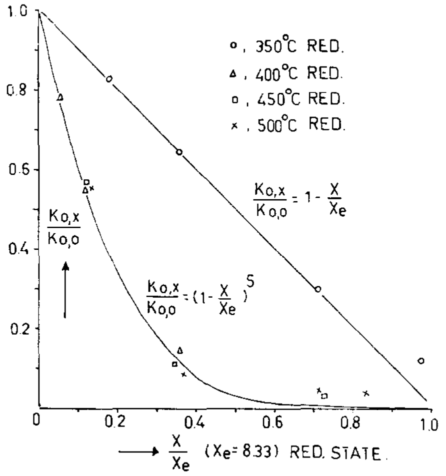


FIG. 4. Dependency of the rate constant (k_0) of the reaction with butene on the degree of reduction X.

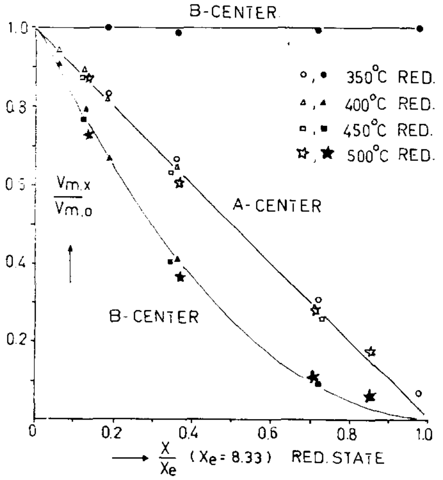


FIG. 3. Dependency of the maximum volume of adsorption (V_m) on the degree of reduction (X).

2. *Properties of Sintered Samples*

a. Decrease of surface area as a function of sintering temperature and time. The area of samples preheated at 500°C is around 3.5 m^2 g^{-1}. A treatment at higher temperatures leads to a pronounced de-

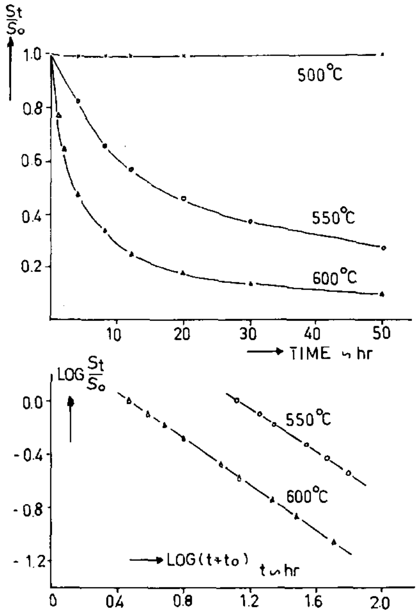


FIG. 5. Rate of the decrease in surface area as a function of sintering temperature and of sintering time.

crease, both as a function of time and temperature of preheating. This diminution can be described by the equation:

$$\log(S_t/S_0) = C - \log(t + t_0) \qquad (2)$$

where S_t and S_0 are the areas at time t and $t = 0$, C and t_0 being constants (Fig. 5).

b. Adsorptive properties (Figs. 6, 7). The maximum volume of the adsorption of butadiene (strong adsorption = A-sites) decreases linearly with the surface area so

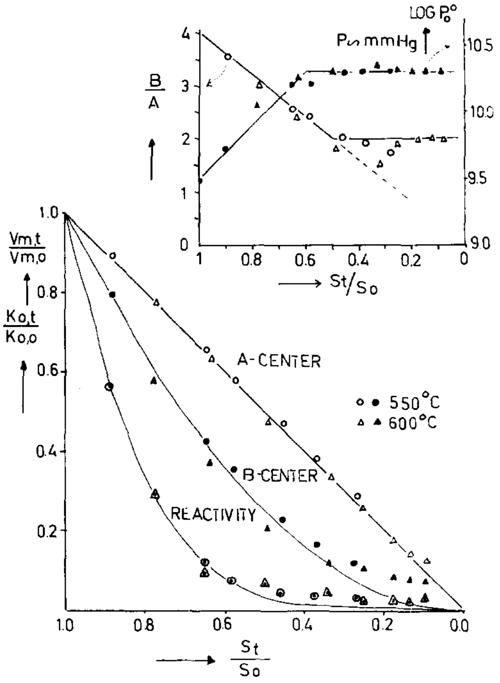


FIG. 7. Dependencies of maximum volumes of adsorption (V_m), of reaction rate constant (k_0) and of the B/A center ratio on the degree of sintering (S_t/S_0) of the catalyst.

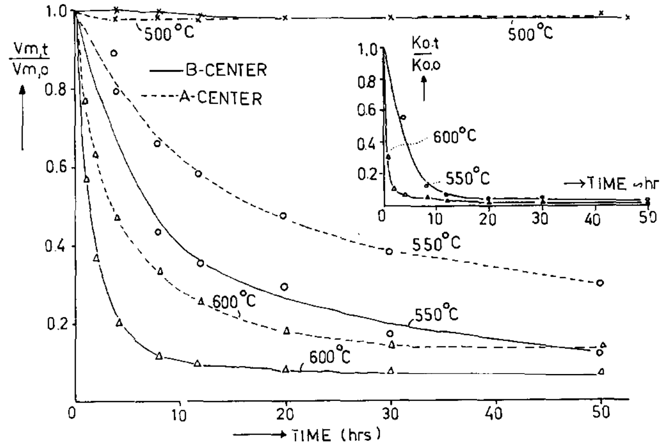


FIG. 6. Rate of the decrease of maximum volume of adsorption (V_m) as function of sintering temperature and time. The decrease of reaction rate constant (k_0) as function of sintering time at two different sintering temperatures.

that the site density remains a constant. The adsorption was only followed for one temperature of adsorption and there is, hence, no information on a possible change of its parameters. The impression was formed that the adsorption became stronger the more advanced the process of sintering. The adsorption of butene decreased in a more pronounced manner with decrease in surface area, and the B-site density (number per unit surface area) falls to about half its initial value. Its parameters were investigated as a function of the degree of sintering. It remains a dual-site type of adsorption over the whole range and the heat of adsorption also remains approximately constant at 12 kcal mol^{-1}. However, the $p_0{}^0$-value is increased; therefore the adsorption entropy changes in the sense that the entropy becomes more negative (from −43 to −48 cal/°; see Fig. 7). The fall in the surface area and in the B-site concentration appear to be unrelated; the surface area continues to decrease after the B-site density and also the newly acquired properties of the B-site have attained their final value.

c. Reactivity. The combination of the decrease in surface area and the diminution in B-site density is seen from Figs. 6 and 8 to result in a pronounced fall in the reactivity, a fall that is particularly evident in the first stages of the sintering process. Quantitatively the decrease in k_0 appears in agreement with the proposal that the active site is a cluster of one A- and two B-sites. As a consequence, the activity of a Bi_2MoO_6 sample decreases by a factor of 40 after heat treatment at 600°C. Since this also should apply for the catalytic activity, the conflicting data on the activity of the koechlinite modification becomes easier to understand.

3. *Errors in the Measurements*

To enable a judgment as to the accuracy of the measurements Table 1 gives estimates of the errors arising from various single factors and of their combination.

DISCUSSION

The results summarized in Fig. 1 show that the rate of reoxidation of a fully reduced Bi_2MoO_6 sample with composition $Bi_2MoO_{5.5}$ depends on the temperature and time to which it has been exposed before O_2 is admitted. This explains the previous discrepancy between the data of Batist and Prette (*6*) and our first results as originating from a different method of pretreating the reduced catalyst. Another conclusion that can be drawn from these results

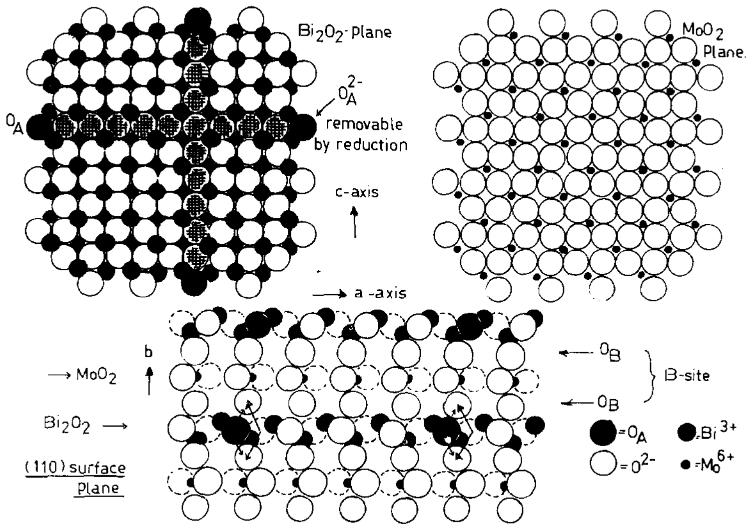


FIG. 8. The surface boundary plane (110) of $Bi_2O_3 \cdot MoO_3$.

TABLE 1
LIMITS OF ERROR IN THE ADSORPTION MEASUREMENTS

Pressure ranges (mm Hg)	Pressure determination[a]	Volume calibration[a]	Temperature change determination[a] ± 0.5°C	Catalyst sample	Total error (%)
10^{-3}–10^{-2}	0.1	0.1	0.3	4	4.2
10^{-2}–10^{-1}	0.2	0.1	0.3	4	4.3
10^{-1}–1	0.8	0.2	0.3	4	5.0
1–10	1.4	0.4	0.3	4	5.9

[a] Errors in single readings during adsorption (%).

is that the change in behavior of samples pretreated in a different manner is entirely due to a rearrangement in the bulk structure. This is facilitated by the application of higher temperatures either during the reduction or during evacuation of the reduced sample, it being immaterial whether the higher temperature is applied in the first or the second stage. The higher the temperature the more difficult it became to reoxidize the sample. The rearrangement of the bulk structure is accompanied by a change in the surface structure. Samples that were reduced and evacuated at 350°C only lose O_A sites. At 400°C the B-sites also are eliminated and at still higher temperatures a new phenomenon developed: the catalyst begins to adsorb O_2 at lower temperatures according to a weak type of adsorption involving molecularly adsorbed oxygen. The maximum amount adsorbed is about double that of the B-sites, i.e., 0.2 $cm^3\ g^{-1}$. Since a B-site contains two oxygens (O_B), a vacancy left by the removal of one O_B might presumably adsorb one O_2 molecule. However, the temperature of disappearance of O_B does not coincide with that leading to the appearance of the weak O_2 adsorption. Thus, O_B is first deactivated, for instance by the reduction of Mo^{6+}, to which it is connected, and later on diffuses into the interior, or it is another type of oxygen O_C that begins to migrate at the higher temperatures. Independent of the solution of this problem we have to assume that the internal change in the bulk tends to inhibit a diffusion process, operative for samples reduced at lower temperatures.

These experiments also allow an insight into the structure of the reactive site. Samples reduced at 350°C show a dependency of O_A and k_0 (the frequency constant) with $n = 1$ [Eq. (1)] and the site therefore contains one O_A. If reduced at higher temperatures the density of B-sites follows $n = 2$ [Eq. (1)] but that of k_0 is found to give $n = 5$. Therefore the reactive R-site is a cluster of one O_A and two B-sites (or 4 O_B).

The next item concerns the sintering of fully oxidized Bi_2MoO_6. The decrease in surface area S as a function of sintering time was given by Eq. (2) which can be derived from the differential equation:

$$-dS/dt = k_s \cdot S^2 \tag{3}$$

with the boundary conditions: $t_0 = 1/S_s \cdot k_s$ and $\log t_0 =$ constant. The temperature dependency of the "reaction constant" k_s, if represented as:

$$k_s = k_{0,s} \cdot \exp(-E/RT) \tag{4}$$

shows E to be ~40–45 kcal.

From Fig. 7 we see that the number of A-sites decreases linearly with the surface area so that its surface concentration remains invariant. This shows this concentration to be more than an accidental value and to be connected intrinsically with the surface structure, an observation that will make it necessary to reconsider our model for the form of the crystals. A following observation is that the B-site concentration decreases faster than the surface area, falling to a value about half that of the original. An interesting aspect of this decay is that it occurs at an earlier time than the fall in the surface area and apparently is not directly connected with it. Finally, in excellent agreement with our earlier conclusion, we notice that the reactivity, measured as k_0, decreases very sharply. The decrease is far from linear with that of the surface area and actually in good agreement with the supposition that the reactive site consists of one O_A and two B-sites. This explains the conflicting evidence in the literature as to the catalytic activity of the koechlinite modification; the activity is strongly dependent on the calcination temperature.

We shall now try to explain our observations in terms of the Zemann structure of koechlinite (*2*). In a simplified form this structure consists of layers of Bi_2O_2 (similar to those encountered in BiOCl) and of layers of MoO_2, interconnected by oxygen layers in such a way that the Mo^{6+} ions are octahedrally surrounded by oxygen, the octahedra sharing corners (see Figs. 8, 9). There accordingly exist three crystallographically different types of O ions, viz., O_I in the Bi_2O_2 plane, O_{II} in the MoO_2 plane and O_{III} in the interconnecting oxygen layers, their bulk concentrations being equal. Reduction of the compound leads to a removal of one out of every twelve oxygens and one of the three groups must therefore consist of two subgroups, one that cannot be removed by reduction and another that can, their concentration ratio being 3:1. There is no obvious reason for this subdivision although it may perhaps have to do with a detail in the structure discussed already by Zemann. The Bi_2O_2 planes in koechlinite are somewhat different from the ideal situation as encountered in BiOCl where they are flat. In koechlinite one observes an orthorhombic distortion either because some of the oxygens are bent out of the plane or because planarity is maintained by the occurrence of two different Bi–O distances. The distortion probably finds its origin in a slight misfit between the Bi_2O_2 and MoO_2 planes. Leaving aside the origin of the subdivision we notice however that reduction starts from A-centers and leads to the removal of the bulk oxygens. Since in our earlier paper we located the A-centers at the edges of the Bi_2O_2 planes it is logical to place the reducible oxygens also in these planes. Because only one out of four of these oxygens is removable only one out of four of the supposedly similar oxygens at the Bi_2O_2 edges should be removable and it is only then that it is an O_A. The small surface concentration of O_A is thus accounted for. The actual situation at the surface depends on the choice of the crystallographic planes that form the boundary faces.

In our former model we assumed a crystal of the catalyst to be tabular in habit, the top and bottom faces being (010) planes, therefore either Bi_2O_2 or MoO_2 planes, while the edges were either (110) or (111) planes, the reactive sites being located at the edges. It has been shown that this is a less attractive model and we shall, therefore, assume that an average catalyst crystal possesses only (110) or (111) faces.

The situation for a crystal entirely formed from (110) planes is given in Fig. 8. For the Bi_2O_2 plane we see that the edges are formed from alternating vacancies and oxygens, each vacancy and oxygen belonging to a pair of Bi ions. The edge oxygens should form the O_A. To account for the fact that only one in four is active as such and that it causes the corresponding bulk oxygens to be reducible, we introduce reducible and nonreducible rows of oxygens in the bulk, the reducible rows being connected with an O_A at the surface. We have done this in a symmetrical manner for the sake of simplicity, i.e., in the directions of the *a*- and *c*-axes one in eight rows and, therefore, one in four surface oxygens is removable. A more real solution would perhaps have been to limit these rows to one direction so that O_A would only have been present on two of the sides of the square instead of on four but then in greater density.

At the MoO_2 plane every surface Mo^{6+} is connected with a vacancy and therefore in a square pyramidal situation. Such a Mo is of course connected with two O_{III} ions at the surface. If we now identify the arrangement (O_{II}–vacancy over Mo–O_{III}) as a B-site we see that the surface situation possesses four B-sites for every O_A. The situation for a location of the plane edges in accordance with (111) as the boundary planes is somewhat different (see Fig. 9). At the Bi_2O_2 edges of the surface Bi ions, one is connected to a vacancy and the other to a surface oxygen. Again, selecting one in every eight rows to be removable, we find one in every four surface oxygens to be O_A, their surface concentration being similar to that on the (110) plane. However, the edges of the MoO_2 planes now consist of alternating square pyramidal (i.e., attached to a vacancy) and octahedral (i.e., covered by a surface oxygen) molybdenum ions. If only the first category is counted as giving rise to a B-site, the concentration of B-sites is half that on the (110) plane. We may, therefore, account for the change in surface situation as a consequence of sintering: it might be a reorientation from (110) surface planes to (111) planes. The change is not only in the number of sites. Since the parameters of the butene adsorption change somewhat (increase of ΔS_{ads}) the character of the B-sites is also somewhat different. Actually they have been rotated over $\pi/4$ which might involve a change in their adsorption behavior.

The phenomena during bulk reduction and reoxidation find a simple explanation in this model. Reduction at 350°C removes the oxygens from the active rows in the Bi_2O_2 planes and reoxidation starts at the A-vacancies to fill these rows again by diffusion into the interior. At temperatures above 400°C, however, the rows are filled from the layers above and below the Bi_2O_2 layers, initially from the O_{III} group and later perhaps from the MoO_2 layers (O_{II}). Reoxidation has now to follow another diffusion path (even more important) a different port of entrance. At the vacancies derived from these sites adsorption appears to be an activated process and a new type of reoxidation kinetics is observed. Evidently, this change in bulk structure is connected with a transfer of charge. In the low temperature state the Bi ions are the cations that become reduced but during the conversion to the high temperature situation the negative charge is undoubtedly transferred to Mo ions.

The new data allow us to present a somewhat more detailed picture of the site responsible for the actual catalysis. We now know with reasonable certainty that the R-site is a cluster of one O_A and two B-sites but this statement needs further clarification. It could, for instance, mean that the site is a combination of O_A and

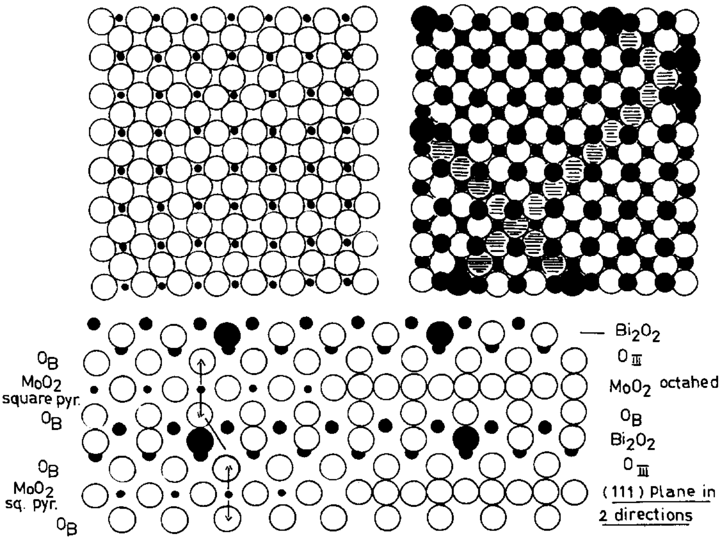
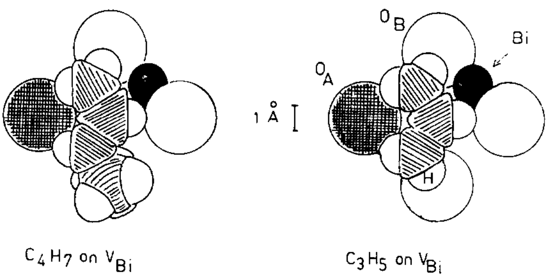


FIG. 9. The surface boundary plane (111) of $Bi_2O_3 \cdot MoO_3$.

four O_B; we have originally considered this the most attractive solution. However, the surface model given above shows that it is incorrect. It is not difficult to find situations where combinations of this kind occur, but invariably the four O_B then belong to four and not to two B-sites and this solution therefore is excluded. The minimum and maximum number of O_B are, respectively, two and four but in both cases they should belong to two B-sites.

In further constructing the site, results from earlier workers in the field should be taken into account. There is, firstly, the important conclusion of Adams and Jennings (*4*) from their study of the kinetic isotope effect of the propene oxidation over Bi-molybdate catalysts, i.e., that the abstraction of the first hydrogen is rate determining, which means that (a) the reaction occurs in steps and is not "concerted," and (b) that it involves an allyl intermediate. Secondly there is the unanimous conclusion of various groups of workers (*8–11*) from isotopically marked propene that the allyl intermediate should be bonded in such a position at the surface that the terminal C-atoms of the allyl group are equivalent. This almost certainly excludes σ-bonding to oxygen atoms as the relevant intermediate. However, this bonding has been shown by Fahrenfort and Sachtler (*12*) to be present for the oxidation of benzaldehyde, and also our measurements on the adsorption of 1-butene can hardly be explained otherwise than by accepting such an intermediate. In the latter case this particular kind of allyl is excluded as rate determining on the argument that its formation is very fast.

In short we are in need of a second type of adsorbed allyl that is (a) much more difficult to form, and (b) that is symmetric. We now propose that the rate determining reaction leads to the formation of an allyl bonded to a vacancy on the Bi_2O_2 edge (V_{Bi}) situated next to an O_A. The position of these vacancies is indicated in Figs. 8 and 9 and it can be observed that they have two O_B's, belonging to two different B-sites as nearest neighbors. In Fig. 10 an allyl (C_3H_5 or C_4H_7) is shown in a position with the plane of the C-atoms parallel to the surface. A C_3H_5 intermediate is then in a position with the terminal C-atoms symmetrically oriented with respect to O_A. A C_4H_7 group can have its terminal CH_3 group precisely above one of the neighboring O_B's, i.e., a favorable situation to donate a H atom to this O_B. We can now describe the situation giving rise to the formation of the reactive allyl with help of Fig. 11, where *X* is the activated complex, that actually consists of a H-atom (proton) moving to an oxygen ion belonging to the first B-site and an allyl in the act of becoming attached to a V_{Bi}. In the formalism of the absolute rate theory this transition state is in equilibrium with the initial state. Therefore these two states, namely the initial and the transition state, determine the observed isotope effect. However, a state in which the olefin is adsorbed on the B-site to which belongs the oxygen potentially able to accept the proton, is also



C_4H_7 on V_{Bi}

C_3H_5 on V_{Bi}

FIG. 10. Adsorption model of propene and of butene in the form of an allyl complex on a vacancy (V_{Bi}) on Bi at the Bi_2O_2-edge.

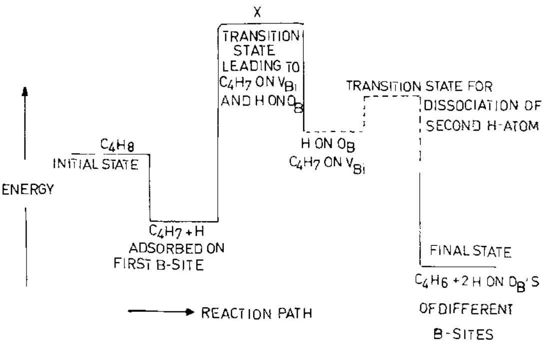


FIG. 11. Energy diagram for butadiene formation from butene on Bi_2MoO_6.

in equilibrium with the initial state and consequently with the transition state. Although it is immaterial to the kinetics of the system whether the activated complex is formed directly from the gas phase or via the intermediate adsorbed state we might still describe the reaction in the latter manner. The reaction could then be visualized as follows: Adsorption of olefin on B-site → activated complex → adsorbed state in which a proton or H-atom is on an oxygen belonging to this B-site but the allyl is on V_{Bi} → dissociation of the second H-atom to an oxygen belonging to a second B-site → desorption of butadiene. The final process, i.e., the desorption of H_2O, occurs because the H-atoms migrate to an O_A.

Formally we could write the reaction sequence as follows:

1) $$\mathrm{C_4H_8 + Mo^{6+} + 2O_{B1}{}^{2-} \rightarrow (C_4H_7O_{B1})^- + (O_{B1}H)^- + Mo^{4+}}$$

2) $$\mathrm{(C_4H_7O_{B1})^- + V_{Bi} + Mo^{4+} \rightarrow Mo^{6+} + (C_4H_7)^-Bi + O_{B1}{}^{2-}}$$

rate determining reaction

3) $$\mathrm{(C_4H_7)^-Bi + O_{B2}{}^{2-} \rightarrow (C_4H_6)^{2-}Bi + (O_{B2}H)^-}$$

$$\mathrm{(C_4H_6)^{2-}Bi \rightarrow Bi^+ + C_4H_6}$$

4) $$\mathrm{(O_{B1}H)^- + (O_{B2})^- + O_A{}^{2-} \rightarrow H_2O + V_A + O_{B1}{}^{2-} + O_{B2}{}^{2-}}$$

where $O_{B1}{}^{2-}$ and $O_{B2}{}^{2-}$ are oxygen ions belonging, respectively, to B-site number 1 and 2. V_A is vacancy left after removal of O_A.

For the oxidation of propene, reaction 3 would be:

$$\mathrm{(C_3H_5)^-Bi + O_{B1\,or\,2}{}^{2-} \rightarrow (C_3H_4)^{2-}Bi + (O_{B1\,or\,2}H)^-}$$

$$\mathrm{(C_3H_4)^{2-}Bi + 2Bi^{3+} + O_A{}^{2-} \rightarrow C_3H_4O + V_A + 2Bi^+}$$

It should be stressed in this connection that the manner of expressing allyl intermediates as a positive or negative entity only serves to account for the number of electrons involved and that it is not meant to indicate that at any time of the reaction these positive or negative entities are indeed present. In fact during the conversion these electrons are highly delocalized over the cations Mo^{6+} and Bi^{3+}.

This new model can also explain the *isomerization of the butenes*. Batist, Van der Heiden and Schuit (*13*) observed that the oxidation and isomerization are intimately connected: for instance, they are both inhibited by butadiene and NH_3. We have shown earlier that the inhibition by butadiene is caused by a slow but strong adsorption on O_A and have in fact applied this property to identify and measure O_A. A blocking of O_A is obviously equivalent to the inhibition of reaction 3 as far as the oxidation is concerned but it is less obvious for the isomerization that does not need this reaction. The explanation given earlier was that isomerization needed migration of hydrogens and that this should occur via O_A. However, the model proposed here allows a somewhat different explanation. If reaction 1 occurs while there is a proton on O_{B2} because of another adsorbed butene, interaction of the allyl formed in 3 with this proton could lead to an isomerization with the proton attacking the allyl from a different position. Hence, after reaction 1 the following could happen:

5) $$\mathrm{Mo^{6+} + C_4H_8 + 2O_{B2}{}^{2-} \rightarrow (C_4H_7O_{B2})^- + (O_{B2}H)^- + Mo^{4+}}$$

representing the adsorption of a second butene molecule.

6) $$\mathrm{Mo^{4+} + (C_4H_7)^-Bi + (O_{B2}H)^- \rightarrow C_4H_8 + Mo^{6+} + O_B{}^{2-} + V_{Bi}}$$

isomerization.

That this reaction is faster than the oxidation indicates that the formation of $(C_4H_7)^-$Bi is facilitated by the presence of a proton on the neighboring O_B, a proposition not altogether unreasonable. Moreover, the inhibition of the isomerization by butadiene proves that the inhibition process is connected with a steric effect, access to V_{Bi} being blocked by the presence of a butadiene molecule on the neighboring O_A.

The Zemann structure has thus been shown to be of great value in understanding the catalytic phenomenon. In one particular aspect, however, it appears to leave us in the dark: it does not present a satisfactory explanation for the partial reduction and (presumably related with it) for the low surface density of O_A. This is a point of considerable importance since it is undoubtedly connected with the selectivity of the catalyst and therefore merits further study.

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