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Active Sites for Reactions of Olefin Molecules at Surfaces of Molybdate Catalysts

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Oxidation of propene, 1-butene, and isobutene by gas-phase oxygen was studied on catalysts prepared by impregnation of MoO_3 with varying amounts of Bi^{3+} and Fe^{3+} ions. Experiments with MoO_3 platelets revealed that Bi^{3+} ions are deposited selectively on (100) and (001) crystal planes, where OH groups are present, but not on the (010) plane. Such impregnation may be called crystallographically specific. At low coverages the yield of acrolein was proportional to the surface concentration of Bi^{3+} ions, which indicates that individual Bi^{3+}–oxygen polyhedra function as centers activating hydrocarbon molecules, the turnover being 1 propene molecule per Bi^{3+} ion per pulse. The yield of CO_2 remained constant, showing that it is formed in a parallel reaction involving centers activating oxygen molecules. Isobutene behaved similarly, whereas 1-butene gave only butadiene because of the competition between second hydrogen abstraction and oxygen addition. Fe^{3+} ions activate oxygen but not hydrocarbon molecules, increasing total oxidation. In the presence of ammonia, O^{2-} ions at the MoO_3 surface are replaced by NH^{2-} which then make a nucleophilic attack on allyl species generated on Bi^{3+} active centers.

INTRODUCTION

It is now generally accepted (*1–3*) that catalytic reactions of selective oxidation of hydrocarbons on oxide catalysts start with activation of the hydrocarbon molecule, followed by a series of consecutive elementary steps of hydrogen abstraction and nucleophilic oxygen addition. For alkenes, activation consists of α-hydrogen abstraction to form an allylic intermediate, and this is usually rate determining.

However, in contrast to metal-on-carrier catalysts where turnover frequencies can be determined and used to characterize the specific activity of these catalysts, such determination has never been carried out for hydrocarbon oxidation reactions on oxide catalysts. On the one hand, these reactions are usually multistep processes requiring the participation of a number of different active centers on the oxide catalyst and it is difficult to investigate these steps separately. On the other hand, even if the particular active centers could be identified, it has not been possible to determine their number.

Results of many studies (*4–6*) clearly indicate that in the case of molybdate catalysts the activation of olefin molecules takes place at cationic sites such as Bi^{3+}, Ni^{2+}, Co^{2+}, of $Bi_2(MoO_4)_3$, $NiMoO_4$, $CoMoO_4$, etc., catalysts, respectively. If a known quantity of these ions were supported as isolated cations at the surface of a carrier and if a method were available to measure the number of olefin molecules activated by these ions, i.e., the number of allylic species generated in unit time, the turnover frequency of the centers active in selective oxidation of olefins could be determined. It should be remembered at this point that allylic radicals, when brought into contact with the surface of MoO_3 under appropriate conditions, extract oxygen and are selectively coverted to acrolein (*4*). MoO_3 may thus serve as a probe to detect activated propene molecules, with the

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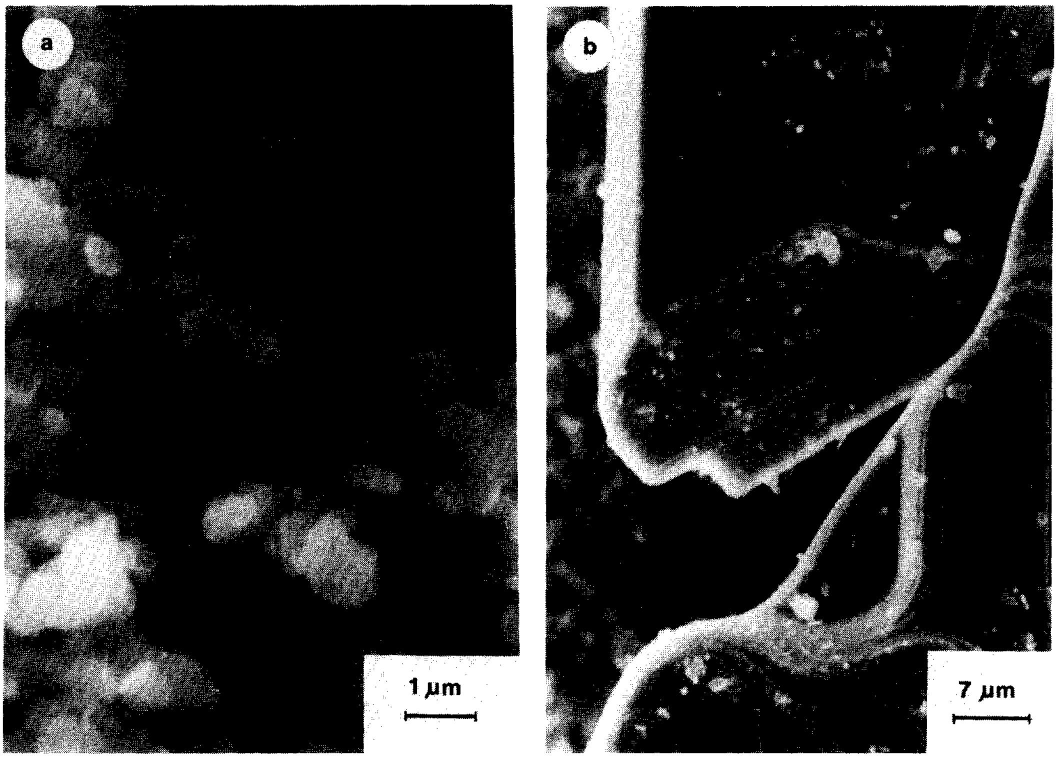


FIG. 1. Scanning electron micrographs: (a) powdered MoO_3 (Climax Molybdenum Co.); (b) plate-like crystallites obtained by sublimation.

amount of acrolein formed being used as a measure of the number of activated propene molecules.

In line with these ideas, isolated bismuth ions were supported at the surface of MoO_3 and their catalytic properties in the oxidation of olefins were studied.

EXPERIMENTAL

Materials. MoO_3 was supplied by Climax Molybdenum Company; its surface area, determined by the BET method from low-temperature krypton adsorption, was 2.59 m^2/g. It was a powder material composed of small crystallites approximately spherical in shape (Fig. 1a). In some experiments, large plate-like crystallites of MoO_3, exposing the basal (010) plane, were used. These were obtained by sublimation of MoO_3 (Climax Molybdenum Co.) at 1073 K in a tubular furnace in a stream of air; the resulting crystals were about 10 mm long, 3 mm wide, and a few tens of micrometers thick (Fig. 1b). Bi^{3+} ions were supported on the MoO_3 surface by impregnation from a solution of $Bi(NO_3)_3 \cdot 5H_2O$ in nitric acid (pH ~ 1.9–2.0) at room temperature. In the case of impregnation with Fe^{3+} ions, an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$, pH ~ 7, was used. MoO_3 was mixed with a volume of the solution sufficient to form a slurry. A Bi^{3+} or Fe^{3+} concentration of 5×10^{-1} to 5×10^{-3} M was chosen so that the solution taken to prepare the slurry contained the amount of metal ions required to produce the desired surface coverage of MoO_3. The slurry was first slowly dried at room temperature with continuous stirring and then dried at 140°C for 10 h. Finally, the samples were calcinated at 500°C for 5 h in air.

It may be assumed that Bi^{3+} ions exchange during impregnation with the appropriate number of protons at the surface of MoO_3. Their average surface concentration may be estimated to be $5 \times 10^{18}/m^2$ (see below). If it is assumed that each Bi^{3+} ion neutralizes three surface protons, a concentration of 1.7×10^{18} Bi^{3+} ions/m^2 may be taken as equivalent to one monolayer. Thus, a sample with 0.5 monolayer of Bi^{3+} ions supported on MoO_3 and denoted as $0.5Bi/MoO_3$ contains, at the surface, 0.85×10^{18} Bi^{3+} ions/m^2, which is equivalent to one-sixth of the OH groups at the MoO_3 surface.

XPS analysis was carried out with a Vacuum Generator ESCA3 apparatus with X-ray excitation from Al (1486.6 eV). Specimens were deposited from an acetone suspension onto a copper sample holder. As the thin layers of specimens did not completely cover the holder, peaks corresponding to Cu_2O were present in the spectra, manifesting themselves as a broadening of the O 1*s* peak on the lower-binding-energy (B.E.) side. The Au $4f_{7/2}$ peak, assuming its B.E. value to be 84.0 eV, was used as reference; the B.E. of 0 1*s* was then determined to be 529.8 eV. This value was constant within 0.2 eV, indicating that no charging effects appear in the samples. MoO_3 has semiconducting properties and its electrical conductivity is high enough to prevent the accumulation of surface charge. The position of the 0 1*s* peak was then used as an internal standard for determining the B.E. values of Bi 4*f*, Mo 3*d*, and Fe 2*p* electrons. ESCA results for the catalysts are shown in Table 1. The MoO_3 doublet at 231.6 and 234.7 eV, in agreement with earlier measurements (*7*, *8*), is symmetric; this indicates that the surface of MoO_3 is fully oxidized and lower-valent Mo ions are absent. Accordingly, the surface atomic ratio N_O/N_{Mo} assumes a high value of 3.2. The B.E. of the Bi 4*f* electrons corresponds to the 3+ oxidation state (*9*, *10*). It is practically the same for all samples, implying that Bi^{3+} ions are present in the same coordination irrespective of the surface concentration. The B.E. value for Fe 2*p* electrons shows that Fe ions are trivalent.

Procedure. The oxidation of propene, 1-butene (Fluka, purum), isobutene (Fluka, purum), and allyl iodide (Reakhim, purum) was studied with the pulse method. Pulses of either a mixture of 0.3 ml olefin + 0.3 ml oxygen or 0.6 μl of allyl iodide were introduced into a stream of helium carrier gas passing through the catalyst bed (0.5 g) at a flow rate of 30 ml/min. The sample of catalyst was placed in a microreactor connected on-line to a series of gas chromatographs.

TABLE 1

Binding Energies of Bi, Fe, Mo, and O Electrons

Sample	Binding energy, E_B (eV)						I_O/I_{Mo}
	Bi 4*f*		Mo 3*d*		Fe 2*p*	O 1*s*	
MoO_3			231.6	234.7		529.8	3.2
$0.2Bi/MoO_3$	158.6	163.8	231.8	234.7		529.8	3.1
$0.5Bi/MoO_3$	158.5	163.8	231.6	234.6		529.8	3.2
$1.0Bi/MoO_3$	158.4	163.8	232.0	235.1		529.8	3.3
$0.2Fe/MoO_3$			231.6	234.5		529.8	3.1
$0.5Fe/MoO_3$			231.7	234.8	709.7	529.8	3.1
$1.0Fe/MoO_3$			231.7	234.8	709.8	529.8	3.2
$0.2Bi0.2Fe/MoO_3$	158.6	163.9	231.7	234.7		529.8	3.0
$0.5Bi0.5Fe/MoO_3$	158.6	163.8	231.7	234.7		529.8	3.2
$1.0Bi1.0Fe/MoO_3$	158.5	163.8	231.8	235.0	709.6	529.8	3.3

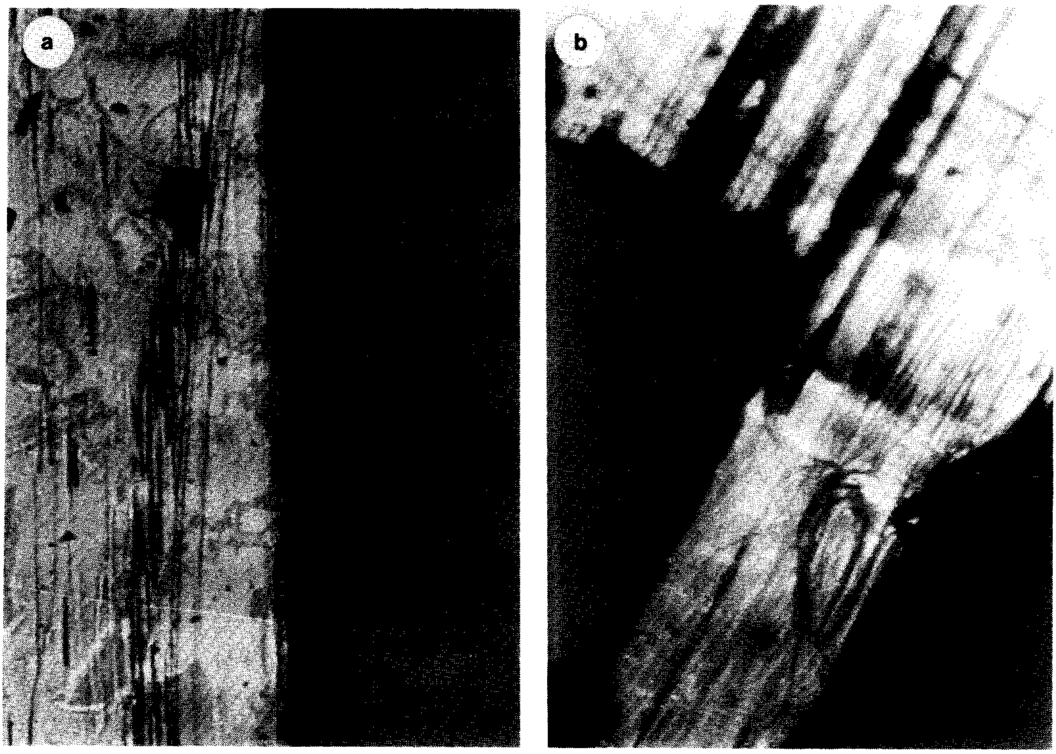


FIG. 2. Micrographs of the MoO_3 platelet after impregnation with Bi^{3+} ions and annealing. (010) plane with (a) (100) edge, magnification 200×, and (b) (100) and (001) edges, magnification 130×.

Liquid products were analyzed using a 2-m Carbowax column and FID. The gaseous products were analyzed on a 4-m column with DMS and a 1-m column filled with molecular sieve 13X; a TDC was used in this case. The oxidation of propene, 1-butene, and isobutene was carried out at 420 and 450°C, whereas the oxidation of allyl iodide was performed at 320°C. With allyl iodide, total conversion is attained at higher temperatures, which makes comparisons among catalyst samples quite meaningless.

RESULTS AND DISCUSSION

Description of the structure of a catalyst obtained by impregnation of a polycrystalline oxide with cations from a solution of the appropriate salts requires answers to two basic questions:

(1) Do the cations uniformly cover the whole surface of the support crystallites or are they adsorbed only on certain planes?

(2) Do the deposited cations remain at the surface of the support or react with the support to form a solid solution or a new phase?

To answer the first question, the following experiments were carried out. Large plate-like crystallites of MoO_3 were suspended in a solution of $Bi(NO_3)_3$ of a concentration sufficient to form a multilayer deposit of Bi^{3+} ions, allowed to stand for 3 h, then removed from the solution, washed quickly with dilute nitric acid, dried at 140°C, and finally annealed at 500°C for 5 h in air. This procedure is similar to that adopted to prepare the powdered samples. Micrographs of two parts of a platelet are shown in Fig. 2 and the electron micrograph of the section at the (100) edge of the platelet is shown in Fig. 3. The basal (010) crystal plane of MoO_3 remained practically unchanged, whereas at the side (100) and

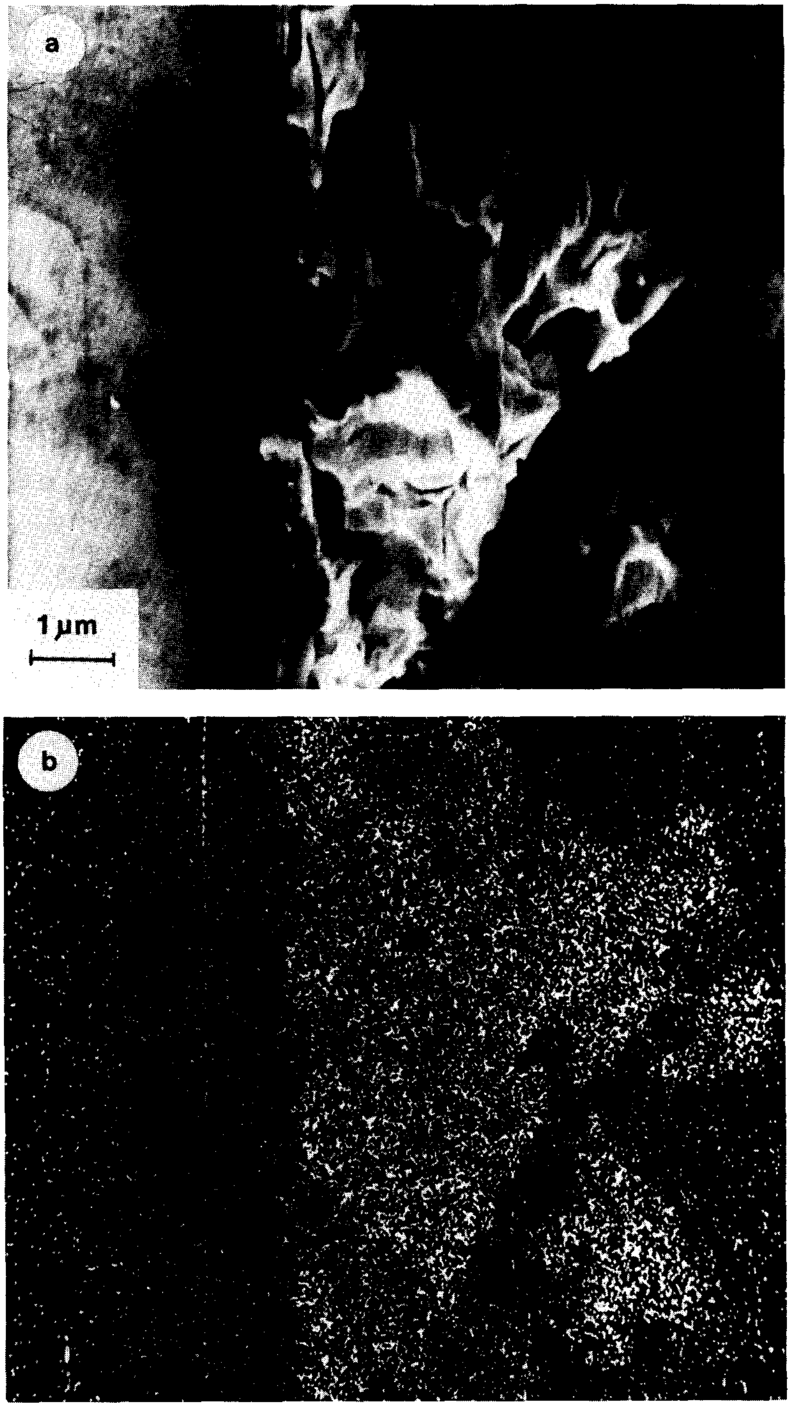


FIG. 3. Electron micrograph of a section of the (100) edge of the (010) plane; (a) scanning, (b) X-ray dot map of bismuth. 1000×.

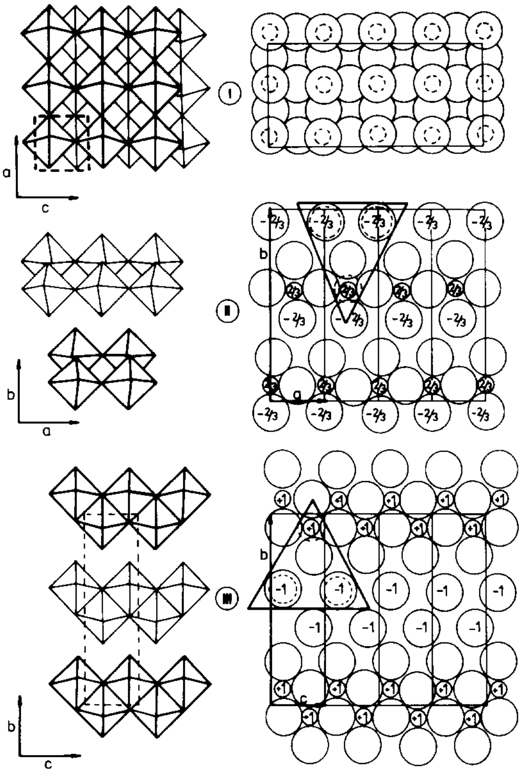


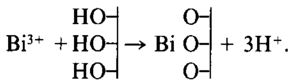
FIG. 4. Idealized MoO_3 structure. Projections: I—(010), II—(001), III—(100). Large circles represent oxygen ions; small circles, molybdenum ions. Solid triangles represent adsorption centers for Bi^{3+} ions; large dotted circles, hydroxyl groups. Numbers represent formal charges of surface ions, positive on molybdenum and negative on oxygen.

(001) planes a new phase is clearly visible. The X-ray dot map (Fig. 3b) shows that this new phase contains bismuth and X-ray diffraction analysis revealed the appearance of a diffraction pattern characteristic of the scheelite structure assumed by the α phase of bismuth molybdate, $Bi_2(MoO_4)_3$. At those locations on the (010) plane where steps and kinks were present, Bi ions were deposited on the (100) and (001) planes exposed at these steps (Fig. 2b).

Thus, the conclusion that may be formulated is that on impregnation no adsorption takes place on the basal (010) crystal plane and bismuth ions are adsorbed selectively only on the crystal faces perpendicular to the basal face, e.g., on (100) or (001). When more than one monolayer of Bi^{3+} ions is deposited at these faces of the MoO_3 crystal, a solid-state reaction takes place on annealing at 773 K, resulting in the formation of $Bi_2(MoO_4)_3$ which is known to be the initial product of the reaction between Bi_2O_3 and MoO_3. This reaction is known to occur around 573 K (*10*). To obtain more information on the mechanism of the formation of this layer product, an experiment was carried out in which the MoO_3 platelets were "immersed" in a crucible filled with Bi_2O_3 powder and the mixture was annealed at 773 K in air for 12 h. After cooling, the MoO_3 platelets could be easily removed from the powder; they showed distinctly visible pits and thin whiskers growing perpendicularly to the surface of (100) and (001) planes. They were very brittle and easily broke away. X-ray analysis of the Bi_2O_3 powder from the vicinity of the MoO_3 platelet revealed the presence of the $Bi_2(MoO_4)_3$ phase of scheelite structure. This indicates that at 773 K the solid-state reaction proceeds through the migration of MoO_3. In the case of impregnated samples, when the amount of Bi ions used corresponded to more than one monolayer deposited at the (100) and (001) crystal planes of MoO_3 crystallites, an outward diffusion of Mo ions took place on annealing, resulting in the transformation of the deposited bismuth oxide layer into $Bi_2(MoO_4)_3$.

MoO_3 has a layer structure in which MoO_3 octahedra are linked together by edges to form a double zig-zag chain; the chains are linked through corners into infinite sheets (*11*). Each octahedron has one unshared corner, the free corners in one layer pointing down between those of neighboring layers. The idealized structure may be considered as fcc oxygen packing with Mo in one-third of the octahedral interstices. The left side of Fig. 4 shows (010), (100), and (001) projections of the arrangement of octahedra, and the right side of Fig. 4 illustrates the idealized arrangement of molybdenum and oxygen atoms on the appropriate crystal planes. On the (010) plane all molybdenum and oxygen ions are coordinatively saturated; therefore, this plane, in the absence of defects, is inert in chemisorption processes. A clean (100) plane contains unsaturated Mo^{6+} ions with one bridging O^{2-} ion missing from their coordination sphere and three types of surrounding O^{2-} ions: 3 bridging oxygens coordinating 3 Mo^{6+} ions, 1 oxygen bridging 2 Mo^{6+} ions, and 1 terminal oxygen with bond order 2 and unsaturated bridging O^{2-} ions with 1 Mo^{6+} ion missing. The formal charge would be 1+ on Mo^{6+} and 1− on unsaturated oxygens. A decrease in local charges could be achieved by dissociative chemisorption of water with a proton going to oxygen and a hydroxyl group being attached to Mo^{6+} ion; this reduces the formal charges to zero. Analogous considerations show that the charges on Mo^{6+} and O^{2-} ions exposed on the (001) plane would be $\frac{2}{3}+$ and $\frac{2}{3}-$, respectively; hydroxylation reduces those charges to $\frac{1}{3}+$ and $\frac{1}{3}-$. It may be calculated from Fig. 4 that the density of hydroxyl groups on fully hydrated (100) planes of MoO_3 should be 7.8 OH/nm^2, and on (001) planes it should be 7.3 OH/nm^2.

It seems plausible to assume that on impregnation in $Bi(NO_3)_3$ solution each Bi^{3+} ion would react with three hydroxyl groups to replace three protons according to the following scheme:



$$\mathrm{Bi^{3+}} + \left.\begin{matrix}\mathrm{HO}-\\ \mathrm{HO}-\\ \mathrm{HO}-\end{matrix}\right] \rightarrow \mathrm{Bi}\left.\begin{matrix}\mathrm{O}-\\ \mathrm{O}-\\ \mathrm{O}-\end{matrix}\right] + 3\mathrm{H^+}.$$

The three OH groups which may be involved in bonding on (001) and (100) planes of MoO_3 are designated in Fig. 4 by large dotted circles and the possible adsorption center for a Bi^{3+} ion is shown by a triangle. The surface concentrations of these centers is 2.6 nm^{-2} on a (100) plane and 2.4 nm^{-2} on a (001) plane. These centers are not present on a (010) plane. If it is assumed that the MoO_3 powder used for the preparation of catalysts is composed of nearly spherical crystallites, exposing (100), (010), and (001) planes in equal proportions, the average surface concentration of Bi^{3+} at complete coverage would be 1.7×10^{18} Bi^{+3} ions/m^2; this value will be defined as the monolayer coverage for powder samples.

Prolonging the duration of impregnation leads to multilayer coverage. It may occur by either adsorption of hydrated Bi^{3+} ions on the adsorbed Bi^{3+} layer, or Bi^{3+} ions may bond to the surface through only two OH^- surface groups, with the residual charge on the adsorbed Bi^{3+} ion generating an adsorption center for the next layer. In either case, monolayer coverage could correspond to a Bi^{3+} concentration greater than that calculated above.

At this point the second question asked at the beginning of this discussion may be raised: do Bi^{3+} ions remain at the surface of MoO_3 in view of the possibility of their diffusing into the bulk during the course of thermal treatment? To answer this question, XPS analysis of the samples was carried out. Figure 5 shows the intensity of the Bi 4*f* peak as a function of Bi^{3+} content. Dotted lines marked λ and 3λ show the dependence of the intensity of this peak on surface coverage calculated under the assumption that Bi^{3+} ions are uniformally dis-

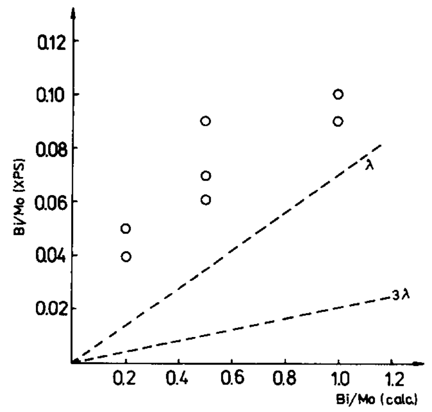


FIG. 5. Results of XPS analysis. Ratio of the intensities of Bi 4*f* and Mo 3*d* peaks as functions of the surface coverage of MoO_3 with Bi^{3+} ions. The dotted lines represent the dependence of the ratio of intensities calculated assuming that Bi^{3+} ions are uniformly distributed in a layer with a thickness corresponding to one-half the escape depth λ of Bi 4*f* electrons, or to 3λ.

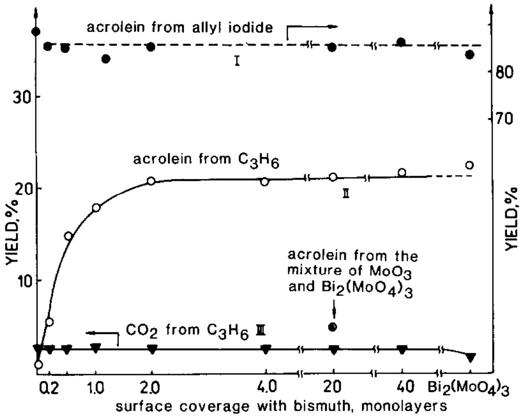


FIG. 6. Yield of acrolein from allyl iodide (curve I) and yields of acrolein (curve II) and CO_2 (curve III) from propene as functions of the surface coverage of MoO_3 with Bi^{3+} ions.

tributed (a) in a MoO_3 subsurface layer with a thickness corresponding to one-half the escape depth of Bi 4*f* electrons (λ) or (b) in a layer three times thicker than that in (a) (3λ). The value of λ is approximately 25 Å. As seen in Fig. 5, the experimental points are located well above the line for λ; this may be taken as an indication that Bi^{3+} ions are indeed located at the surface of MoO_3 crystallites.

The results of the determination of catalytic activity in experiments in which a propene–oxygen mixture of allyl iodide was pulsed over a series of catalysts containing different numbers of Bi^{3+} ions supported at the surface of MoO_3 are summarized in Fig. 6. The yield of acrolein obtained from allyl iodide (curve I) is independent of the number of Bi^{3+} ions and is identical to the value observed for the pure MoO_3. This is in agreement with the earlier conclusion (*4*) that the lattice of the MoO_3 is very efficient in adding oxygen to allyl species once they have been generated, e.g., by decomposition of allyl iodide *in situ* in the catalytic reactor. The amount of acrolein formed by MoO_3 may thus be considered as a measure of the number of allyl species formed as the results of the activation of propene. The presence of Bi^{3+} ions at the surface of MoO_3 does not interfere with the addition of surface oxygen ions to the adsorbed allyl species. This is consistent with the fact that Bi^{3+} ions are deposited at the (100) and (001) crystal planes, and the insertion of oxygen, as shown by our earlier studies (*12*), takes place at the (010) plane.

The yield of acrolien from propene (curve II) is very low in the case of pure MoO_3; this indicates that the surface of this oxide has little ability to activate propene molecules by abstracting an α-hydrogen atom to form an allylic species. For low Bi^{3+} surface coverage, the yield of acrolein increases proportionally to the number of supported Bi^{3+} ions. This indicates that Bi^{3+} ions serve as active centers which convert propene into allylic species. The linear dependence of acrolein yield on the surface coverage of Bi^{3+} ions shows that, at low surface coverage, the activity of these ions is independent of their concentration; i.e., it is the individual Bi^{3+} ions, surrounded by oxide ions, that are responsible for the elementary catalytic step of hydrogen abstraction from a propene molecule. At a surface coverage of about 1.0 the yield of acrolein begins to level off; at a coverage of about 2.0 it attains a constant value that remains unchanged with further increases in the amount of supported bismuth. This can be easily explained by noting that at increasingly higher Bi^{3+} loadings a increasingly thicker layer of bismuth molybdate phase forms on the (100) and (001) planes of MoO_3 crystallites. The surface composition of this bismuth molybdate phase remains unchanged and so do the catalytic properties. Indeed, X-ray diffraction patterns of samples containing an amount of bismuth ions equivalent to a surface coverage greater than five monolayers show the presence of lines characteristic of the scheelite structure of $Bi_2(MoO_4)_3$. The activity of such a Bi_2 $(MoO_4)_3$ layer is independent of its thickness, as shown by the plateau in curve II (Fig. 6) covering a wide range of compositions. Evidence for the sandwich-like model was obtained by an experiment in which catalytic properties were determined for a sample prepared by mixing MoO_3 with crystalline $Bi_2(MoO_4)_3$ in proportions that corresponded to the composition of a Bi^{3+}/MoO_3 sample containing 20 monolayers of Bi^{3+} ions. As seen from the data in Fig. 6, the yield of acrolein obtained from the oxidation of propene over this catalyst was about four times smaller than the yield obtained for the corresponding Bi^{3+}/MoO_3 catalyst. It is noteworthy that the yield of acrolein obtained when propene was oxidized over the $Bi_2(MoO_4)_3$ catalyst, recalculated per unit surface area assuming that Bi^{3+} ions cover two-thirds of the total BET surface area of MoO_3 but saturate the surface in case of $Bi_2(MoO_4)_3$, is the same as that observed for the Bi^{3+}/MoO_3 samples with multilayer coverage; this may be taken as further confirmation of the proposed model.

It should also be noted that the amount of CO_2 formed in the course of the reaction remains constant for all catalysts independently of the amount of Bi^{3+} ions supported at the surface of MoO_3 (curve III, Fig. 6). This clearly indicates that total oxidation of propene takes place at active centers different from those responsible for the activation of propene in the first step of its selective oxidation to acrolein. These centers must be related to some structural defects of MoO_3 itself, and operate independently of the Bi^{3+} ions supported at its surface. The fact that a constant amount of CO_2 is formed although more and more propene is converted to acrolein with increasing Bi^{3+} coverage indicates that CO_2 does not result from the consecutive oxidation of acrolein but is formed in a parallel reaction. The rate of CO_2 formation is not limited by the activation of propene but by the activation of oxygen.

The turnover at one bismuth ion during the passage of one pulse may be calculated by dividing the number of acrolein molecules formed from a pulse of propene, a direct measure of the number of propene molecules activated, by the number of bismuth ions at the surface of a catalyst. The values obtained from a series of experiments in which pulses of a propene–oxygen mixture were injected into a carrier gas flowing with different space velocities over a Bi^{3+}/MoO_3 catalyst (surface coverage equal to 1.0) are summarized in Table 2. It may be seen that the turnover per pulse increases with decreasing space velocity (i.e., increasing contact time); it approaches the value of 1 at longer contact times. This indicates that during the time in which the pulse passes through the catalyst bed, each Bi^{3+} ion can activate only one molecule of propene, i.e., the time required for the reoxidation of the Bi^{3+} active center (the "dead time") must be longer than the

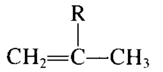
TABLE 2

Oxidation of Propene at Different Space Velocities (1.0Bi/MoO_3 catalyst)

Space velocity (ml/min)	Temperature (°C)	Yield (%)		Conversion (%)	Selectivity (%)		Turnover	
		Acrolein	CO_2		Acrolein	CO_2	Acrolein	Propene
30	420	16.3	2.2	19.1	85.2	11.5	0.30	0.35
	450	19.4	3.6	23.9	81.2	15.1	0.35	0.44
25.5	420	22.7	3.5	25.9	87.7	13.4	0.41	0.47
	450	28.5	4.9	34.7	82.1	14.3	0.52	0.63
21	420	46.3	3.9	51.7	89.6	8.05	0.85	0.94
	450	48.9	5.2	54.4	89.9	9.12	0.89	0.99
15	420	50.6	4.9	56.9	86.9	8.7	0.91	1.04
	450	49.9	7.4	59.0	82.3	13.5	0.90	1.08

time required for passage of the pulse. For a pulse of 0.3 ml C_3H_6 + 0.3 ml O_2 in the reactor used in this study the passage time is 0.6 s; thus, the "dead time" must be longer than this value.

For bismuth molybdate catalysts, Adams (*13*) determined the oxidation behavior for a large number of C_3 to C_8 olefins with various structures. He found that conjugated dienes, where allowed, are preferentially formed as primary products. He also noted that a methyl group attached to a vinyl carbon seemed to be necessary for aldehyde formation. Two explanations for this observation may be considered. The first step of the reaction is common and consists of activation of the hydrocarbon molecule by abstraction of an α-hydrogen to form an allylic intermediate. In the next step, either (1) the abstraction of hydrogen from another carbon, when possible, is much faster than nucleophilic addition of the oxide ion to the allylic species and a diene is formed as the major product, or (2) the steric hindrance and the distribution of electron density prevents nucleophilic oxygen addition except in the case of molecules with a three-carbon atom chain



$$CH_2{=}\overset{\displaystyle R}{\overset{|}{C}}{-}CH_3$$

that allows formation of an allylic species bonded parallel to the catalyst surface, exposing two terminal carbon atoms to nucleophilic attack by oxygen.

To obtain further information pertaining to this question, the behavior of propene was compared with that of 1-butene and isobutene. The former contains the methyl group at the allylic α-carbon and the latter, at the vinyl α-carbon. The results obtained for oxidation of 1-butene (Fig. 7) and of isobutene (Fig. 8) are shown as a function of the surface coverage of MoO_3 with Bi^{3+} ions. The behavior of isobutene is similar to that of propene, whereas in the case of 1-butene only three products were obtained: 2-butene, 1,3-butadiene, and CO_2. Similar products were obtained by Batist *et al.* (*14, 15*) for bismuth molybdates.

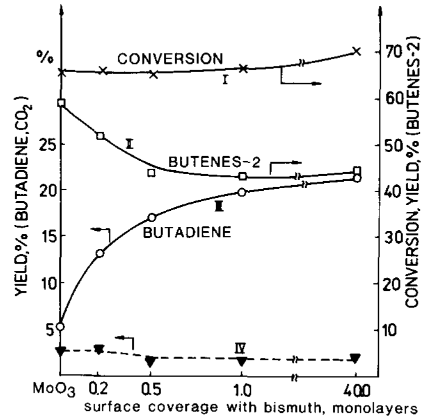


FIG. 7. Conversion for the oxidation of 1-butene (curve I) and yields of 2-butenes (curve II) and butadiene (curve III) as functions of the surface coverage of MoO_3 with Bi^{3+} ions.

Pure MoO_3 is active mainly for alkene isomerization with the amount of oxidation products being very small. Bi^{3+} ions supported at the MoO_3 surface activate 1-butene molecules, enabling initiation of another parallel reaction path. However, in contrast to the behavior of activated propene or isobutene molecules which undergo an attack by oxide ion from the surface of MoO_3 to form acrolein or methylcrolein, respectively, activated 1-butene molecules lose only a second hydrogen atom to desorb as butadiene without the appearance of oxygenated products. 1-Butene and isobutene molecules may be viewed as derivatives of propane, in which the methyl group is substituted at the α- or β-carbon, respectively. It may be assumed that the electron-donating influence of this methyl group on the allylic system formed from either compound would be similar; hence, it could be expected that the charge distribution would render the nucleophilic attack of oxygen equally probable in either case. The difference in behavior of these two compounds must then be attributed to the fact that whenever possible, the abstraction of hydrogen from the second carbon atom is

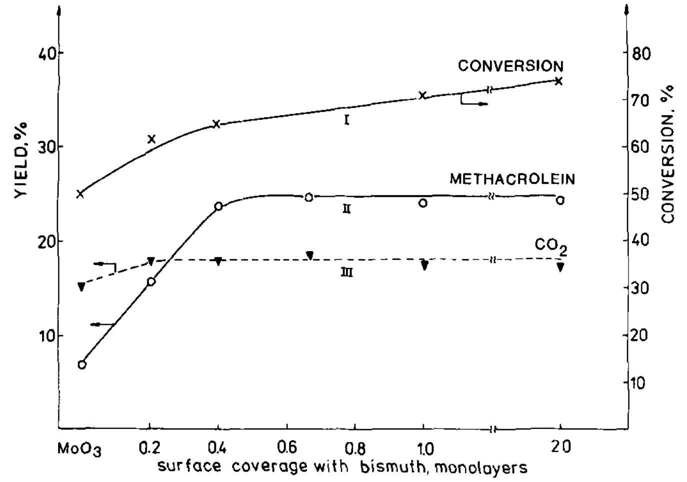


FIG. 8. Conversion for the oxidation of isobutene (curve I) and yields of methacrolein (curve II) and CO_2 (curve III) as functions of the surface coverage of MoO_3 with Bi^{3+} ions.

much faster than the addition of oxygen so that a diene is formed as the main product. This conclusion agrees with the model of Bi^{3+}/MoO_3 catalysts. As shown above, the Bi^{3+} ions that are responsible for activation of the hydrocarbon molecule are located at the (100) and (001) crystal planes of MoO_3, whereas addition of oxygen is performed at the (010) plane. The allylic intermediate must therefore migrate over the catalyst surface if it is to form an oxygenated product; the probability that abstraction of a second hydrogen will occur before addition of oxygen is very high. However, it cannot be excluded that conformation of the organic molecule generates steric hindrance which also contributes to the observed difference in behavior. It is noteworthy that similar to the oxidation of propene, the amount of CO_2 formed from 1-butene is constant and independent of the surface concentration of bismuth. The total oxidation is about the same in both cases; this supports the conclusion that it is the activation of oxygen at some surface defect of MoO_3 that is responsible for the total oxidation of hydrocarbon molecules by a reaction path parallel to selective oxidation.

To obtain more information about the properties that determine the behavior of surface cations as centers for activating hydrocarbon or oxygen molecules, a series of catalysts was prepared by impregnation of the surface of MoO_3 with varying amounts of Fe^{3+}. They corresponded to low surface coverages in the range 0.1–2.0 monolayers so that formation of bulk iron molybdate was not yet observed. In contrast to the results obtained with Bi^{3+}/MoO_3 catalysts, the yield of acrolein is practically independent of the surface concentration of Fe^{3+} ions and the yield of CO_2 rises continuously with increasing coverage of MoO_3 surface with iron ions (Fig. 9). The total conversion

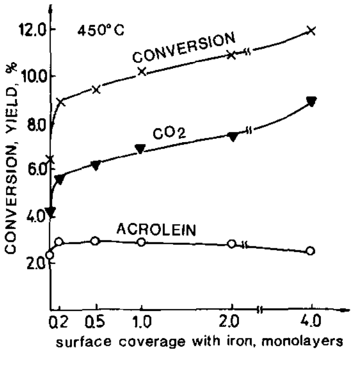


FIG. 9. Conversion for the oxidation of propene and the yields of acrolein and CO_2 as functions of the surface coverage of MoO_3 with Fe^{3+} ions.

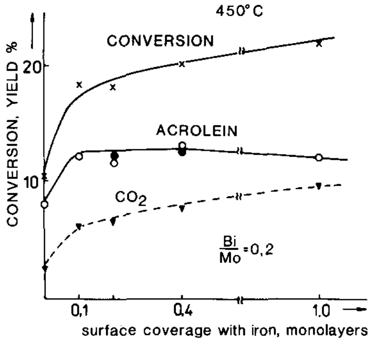


FIG. 10. Conversion for the oxidation of propene and the yields of acrolein and CO_2 as functions of the surface coverage of $0.2Bi/MoO_3$ with Fe^{3+} ions.

is lower with iron-containing catalysts. It may be concluded that iron ions, present at the surface of MoO_3, activate oxygen molecules to increase the activity of the catalyst for total oxidation but have practically no influence on the reaction path which produces partially oxygenated products.

In recent years, many papers (*16–18*) reported that mixed bismuth–iron molybdates are much more active for oxidation and ammoxidation of propene than is pure bismuth molybdate. Several explanations of the activating effect of iron ions in bismuth molybdates have been suggested but the mechanism by which the presence of these ions accelerates the oxidation reaction is not yet clear. It therefore seemed of interest to deposit at the surface of MoO_3 both isolated Bi^{3+} and Fe^{3+} ions and to compare the behavior of such catalysts in the oxidation of propene with that of Bi^{3+}/MoO_3, in which bismuth ions activate the propene molecule, and with Fe^{3+}/MoO_3, in which iron ions activate oxygen molecules. Figure 10 shows data on conversion and acrolein yield obtained on injecting pulses of a $C_3H_6 + O_2$ mixture over MoO_3 catalysts with a surface coverage of Bi^{3+} ions equal to 0.2 and a surface coverage of Fe^{3+} ions varying from 0.1 to 1.0. Addition of increasing amounts of Fe^{3+} ions to MoO_3 results in higher conversion of propene, but only the Fe^{3+} ions added initially increase the yield of acrolein; with further addition of Fe^{3+}, acrolein yield remains practically constant. The two ions seem to operate independently, the property of the system being the sum of the properties of the components. The order of addition of Bi^{3+} and Fe^{3+} to the surface has no effect on the catalytic properties of the samples; this is shown by the results obtained with preparations that were impregnated first with Bi^{3+} ions and then with Fe^{3+} ions (Fig. 10, solid circles) and preparations impregnated first with Fe^{3+} and then with Bi^{3+} ions (Fig. 10, open circles). In Fig. 11 results obtained with the Bi^{3+}/MoO_3 catalysts are compared with those of $Bi^{3+}/Fe^{3+}/MoO_3$ catalysts at equal total metal loadings. Here also, it is only the initially added Fe^{3+} that affects the acrolein yield. It thus appears that the activating effect of iron in bismuth molybdate catalysts is not related to its influence on the electronic structure or the energy of the intermediate complex formed between the reacting propene molecule and the Bi^{3+} active center; it is due to a modification of the properties of the molybdate lattice. Incorporation of Fe^{3+} ions may increase the mobility of oxygen ions in the lattice so that the replenishment of surface oxygen vacancies generated in the course of the catalytic reaction is accelerated; this would shorten the "dead time" of Bi^{3+} active centers.

An interesting question may be raised at this point as to whether the mechanism of

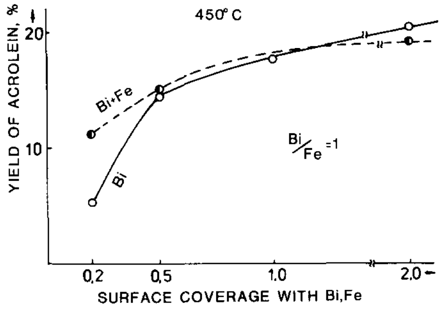


FIG. 11. Yield of acrolein from propene oxidation as a function of the surface coverage of MoO_3 with Bi^{3+} and Fe^{3+} ions. $[Bi^{3+}]_{surf} = [Fe^{3+}]_{surf}$.

TABLE 3

Formation of Acrylonitrile on Catalysts with Different Amounts of Surface Bi^{3+} Ions[a]

Catalyst	Yield of acrylonitrile (%)	Conversion (%)	Selectivity for acrylonitrile (%)	Remarks
MoO_3	3.36	3.7	90.8	
$0.5Bi/MoO_3$	12.3	12.9	95.3	Traces of acetonitrile
$2.0Bi/MoO_3$	16.4	17.0	96.5	Traces of acetonitrile

[a] Conditions 450°C, 0.2 ml C_3H_6 + 0.8 ml NH_3.

activation of propene molecules by Bi^{3+} ions is the same for oxidation to acrolein and ammoxidation to acrylonitrile (*19*). Activity and selectivity data for the reaction of propene and ammonia at the surface of MoO_3 catalysts with different Bi^{3+} surface coverages are shown in Table 3. In all cases, acrylonitrile is formed with very high selectivity and, as was the case for the reaction of propene with oxygen, the conversion increases with the number of Bi^{3+} ions present at the surface of MoO_3. This indicates that Bi^{3+} ions also serve as activating centers for propene molecules in ammoxidation. Table 4 summarizes the results of a series of experiments in which the catalyst was exposed in situ first to a pulse of ammonia, then to a pulse of propene injected after a time interval varying between 3 and 60 s. When propene was injected after 3 s, acrylonitrile was practically the only product. On prolonging the time between the pulse of ammonia and that of propene, acrolein appeared in increasing amounts and, at the same time, the amount of acrylonitrile decreased. However, it is noteworthy that conversion remained constant throughout the whole experiment. These results demonstrate that it is the activation of propene by Bi^{3+} ions that determines the rate of the reaction. On exposing the catalyst to a pulse of ammonia, the surface O^{2-} ions becomes substituted by NH^{2-} groups, which then perform the nucleophilic addition to the allylic species generated by activation of propene molecules at Bi^{3+} active centers. At the reaction temperature of 450°C and in the absence of gas-phase oxy-

TABLE 4

Time lag between NH_3 and C_3H_6 pulses (s)	Yield (%)		Conversion (%)	Selectivity (%)	
	C_2H_3CHO	C_2H_3CN		C_2H_3CHO	C_2H_3CN
3	—	6.92	7.9	—	87.6
15	2.64	4.44	8.0	33.0	55.5
25	4.36	2.81	8.0	54.5	35.1
40	5.95	1.70	8.1	73.5	21.0
60	5.95	1.71	8.0	74.4	21.2

Note. Catalyst: $0.5Bi/MoO_3$. Conditions: 450°C, 1 ml NH_3, 0.3 ml C_3H_6.

gen, the NH^{2-} groups were oxidized slowly by lattice oxygen and removed from the surface in the form of nitrogen oxides, with the vacant surface sites being filled by oxide ions that diffused from the bulk of MoO_3. Thus, on prolonging the intervals between the pulses of ammonia and propene, fewer surface sites were occupied by NH^{2-} groups and more sites were occupied by oxide ions so that the probability of formation of acrylonitrile and acrolein changed accordingly.

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