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Tungsten Oxides as Catalysts in Selective Oxidation

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The reaction of allyl iodide was studied at the surface of four tungsten oxides and molybdenum trioxide. On $WO_{2.95}$ and MoO_3, in which crystallographic shear structures are formed on reduction, acrolein is produced at 300–400°C, whereas $W_{18}O_{49}$ and WO_2, which do not show this property, are inactive, as is WO_3. It is concluded that the transformation of a corner-linked into an edge-linked arrangement of metal–oxygen octahedra provides a facile route for insertion of oxygen into a hydrocarbon molecule.

INTRODUCTION

Some years ago one of the present authors advanced a multicenter model for the selective oxidation of olefins on mixed oxide catalysts (*1–3*). In this it was shown that partial oxidation proceeds in a consecutive series of oxidative elementary steps, each of them requiring different active centers to be present at the catalyst surface. In the first step, in which activation of the olefin molecule takes place, and which consists of the abstraction of α-hydrogen and formation of allylic species, low-valent transition metal cations are involved as active centers. As, however, in the majority of partial oxidation reactions this step is rate determining, studies of these reactions cannot yield any information on the successive stages of reaction. Bypassing the first step by using allyl iodide, which readily decomposes into allyl radicals, showed (*4*) that MoO_3 was able to insert oxygen into the organic species in the second step of the reaction with very high selectivity. It is of some interest to determine which properties of the MoO_3 are responsible for this very high activity and selectivity in the insertion of oxygen.

One of the features common to oxides known to be good catalysts for selective oxidation of olefins is the ability to form crystallographic shear (*CS*) structures (*5, 6*). Removal of oxygen from these oxides results in the formation of edge-linked octahedra characteristic of *CS* planes. It seemed interesting to examine the hypothesis that the easy evolution of oxygen atoms during the transformation from a corner-linked to an edge-linked arrangement of metal–oxygen octahedra may be one of the factors important in enabling these structures to insert oxygen into the organic molecule in hydrocarbon oxidation processes.

The group of structurally complex but well-characterized oxides which form in the tungsten–oxygen system has been chosen for this study. This system has already been studied for the partial oxidation of propylene (*7*) and for propylene and oxygen adsorption (*8*). In the present investigation reactions of allyl iodide, bromide, and oxalate were studied at the surface of two tungsten oxides in which *CS* structures are formed on reduction, namely, WO_3 and $WO_{2.95}$, and two which do not show this property, $WO_{2.72}$ and WO_2. The structures of these oxides are shown in Fig. 1 and full details of the structural characteristics of these materials are given elsewhere (*9, 10*). For purposes of comparison, some experiments were also carried out on MoO_3.

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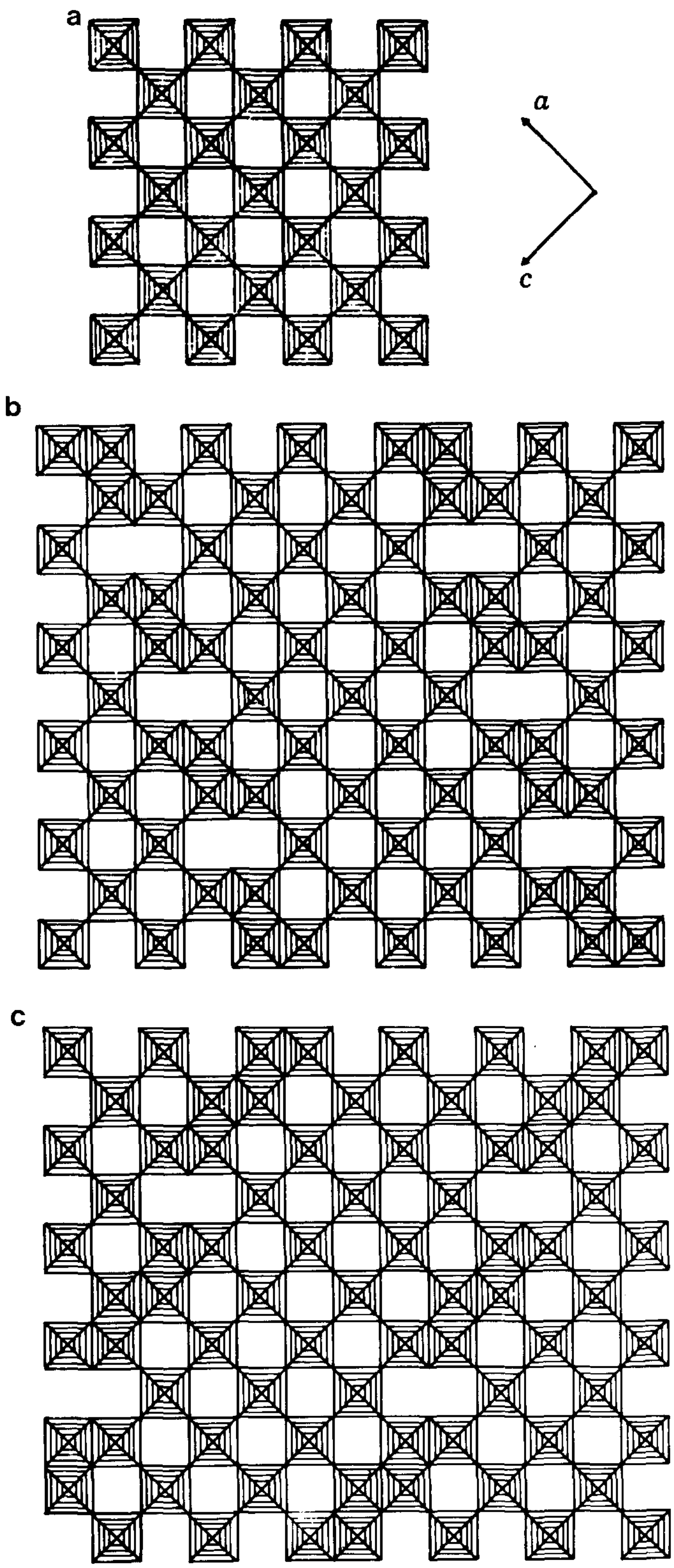
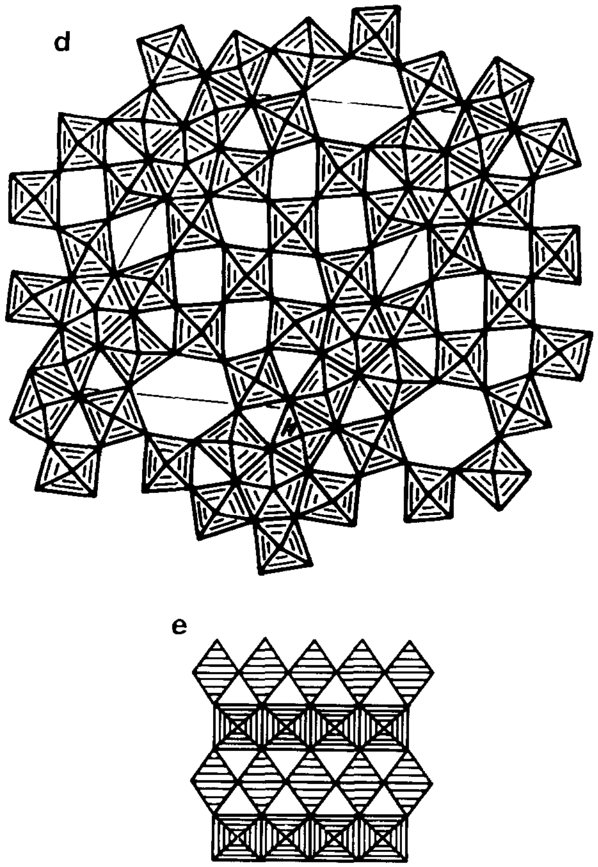


FIG. 1. The structures of the higher oxides studied in this paper. All are composed of linked WO_6 octahedra, which are shown as shaded squares in (a)–(c) and as shaded squares and diamonds in (d) and (e). (a) WO_3, slightly idealized to a cubic form; (b) and (c) a {102} and {103} *CS* plane in reduced



WO$_3$, respectively. The *CS* plane is the part of the crystal containing blocks of four edge-shared octahedra; (d) W$_{18}$O$_{49}$, which contains tungsten in the pentagonal tunnels of the structure and empty hexagonal tunnels as well as WO$_6$ octahedra; (e) Wo$_2$, which has a distorted variant of the rutile structure, the idealized form of which is shown here.

EXPERIMENTAL

Apparatus. The interaction of allyl iodide, bromide, and oxalate (Fluka reagents, pure grade, additionally purified by distillation) with the oxide catalysts was studied by means of the pulse method in a microreactor. Using a microsyringe, 0.5 or 1.0 μl pulses of the liquid reactant were introduced into a stream of 99.99% helium, which was then passed over a sample of the catalyst, placed in the microreactor. Products formed in the course of the reaction were analyzed by gas chromatography using columns directly connected to the output of the reactor. The liquid products were determined on a 3 m column filled with 12% Carbowax on Chromosorb W (for acrolein, benzene, hexadiene) and on a 2 m, 3-mm-diameter column filled with 2% Carbowax and 2% DEGS on Chromosorb W (for acids). The columns were held at temperatures of 80 and 160°C, respectively, and a flow rate of helium of 40 ml/min was employed. Gaseous products (propylene, CO, CO$_2$) were analyzed on a 4 m, 3-mm-diameter column containing DMS at room temperature.

Prior to each set of runs at a given temperature, the samples were heated in helium for 60 min and 5–10 ml of oxygen were introduced in the form of 1-ml pulses. On such a pretreated sample a series of reactant pulses were introduced, and the distribution of products for each pulse was measured. After completing a series of experiments at a given temperature, the samples were subjected to a number of oxygen pulses at a temperature of 460°C in order to burn off any carbon deposit. The amount of CO_2 evolved in this procedure was recorded and the oxygen treatment was continued until no CO_2 was observed. The temperature was then lowered to that of the subsequent measurement, and the sample was kept at this temperature for 30 min in a stream of helium and was standardized by again introducing 10 ml of oxygen. The volume of catalyst was about 0.5 ml, the contact time being about 0.7 sec.

Temperature-programmed desorption (TPD) of the allyl compounds used as reactants was studied in two series of experiments. In the first the reactant was adsorbed at 320°C for 2 min; the sample was then cooled in the reactant vapor to room temperature and stripped with nitrogen as the carrier gas. TPD was then carried out from room temperature to 460°C. In a second series the reactant was adsorbed at room temperature for 60 min; the sample was then stripped with the carrier gas and thermodesorption studied to 460°C. Before each run the sample was standardized by outgassing at 100°C for 60 min and then at 450°C for 30 min.

Materials. The WO_3 and MoO_3 catalysts used were commercial specimens ex Alpha Inorganics (reagent grade). Reduced oxides were prepared by mixing appropriate amounts of WO_3 and W metal ex Johnson Matthey (Specpure grade). The mixtures, well ground, were outgassed in a silica tube at 50–200°C until the vacuum was better than 0.01 N m^{-2}. The silica was then sealed under a dynamic vacuum and the specimen fired at 900–950°C for 3–4 weeks. At the end of the firing treatment the specimens were quenched in water. Transmission electron microscopy and powder X-ray diffraction were used to characterize the samples (*11*). The WO_3, $WO_{2.72}$ ($W_{18}O_{49}$), and WO_2 were all monophasic. The samples of composition $WO_{2.95}$, containing *CS* structures, were never monophasic for reasons which are well known (*9–11*). In the present case the samples contained high densities of {102} and {103} *CS* planes with microstructures typical of these phases. MoO_3 was obtained by thermal decomposition of ammonium paramolybdate at 500°C for 4 hr.

RESULTS AND DISCUSSION

Although the aim of the present study was to attempt to discover the mechanism by which oxygen was inserted into the organic molecules over tungsten oxide catalysts, we should report at the outset that the major product in our experiments was propylene. Indeed, at temperatures above 330°C for WO_3, $W_{18}O_{49}$, and WO_2, and above 350°C for WO_3 and MoO_3, practically total conversion of allyl iodide to propylene was observed, resulting from the homogeneous pyrolysis of allyl iodide successfully competing with the heterogeneous insertion of oxygen. This undesirable situation was mainly due to the short contact time of the reactants with the catalyst and the low total surface area of the catalyst bed. We will not discuss this reaction further in this report.

The reaction of interest in this study is that of oxygen insertion at the catalyst surface to produce oxygenated products such as acrolein, acetone, and methylglyoxal. In this case, two different modes of sample behavior were found. At temperatures below 450°C acrolein was the main oxygenated product. We will refer to this as the low-temperature region. At temperatures above 450°C, the high-temperature region, the main oxygenated product was methylglyoxal. The differences in these two temperature regions is illustrated in Fig. 2, which shows the selectivity of the reaction as a function of the temperature of the reaction and the number of pulses at the given temperature. We will consider only the reaction which produces acrolein, i.e., the low-temperature region, in this paper.

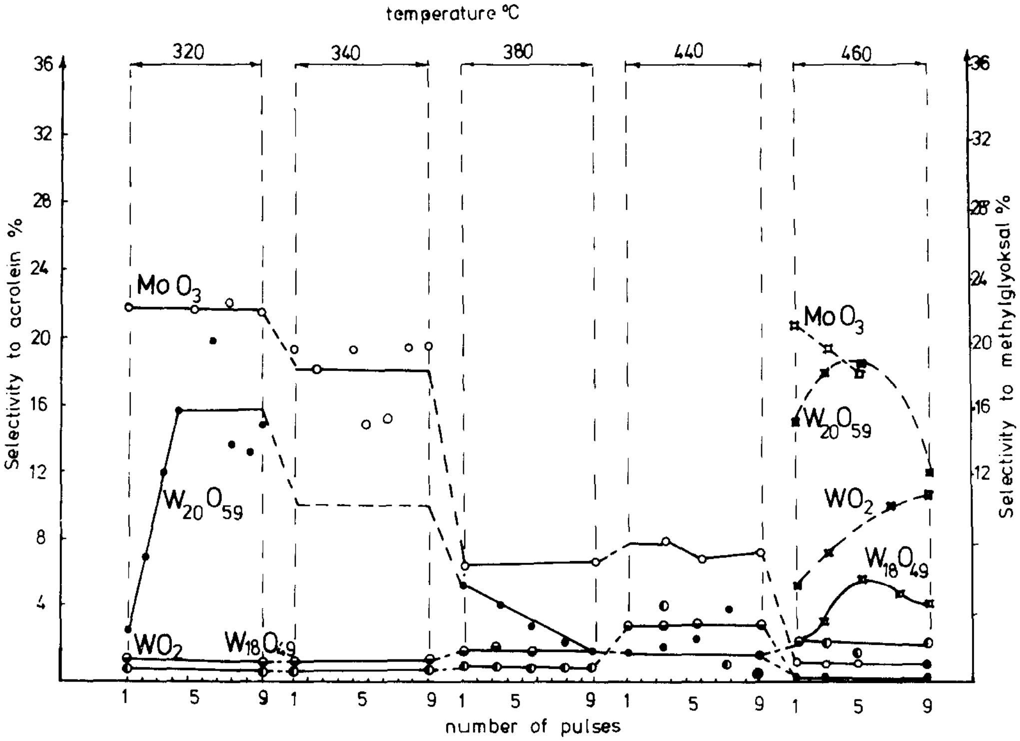


FIG. 2. Selectivity to acrolein and methylglyoxal on reacting allyl iodide with MoO_3 and different tungsten oxides as function of temperature and number of pulses. ○, Acrolein, □, methylglyoxal.

However, we will mention here for completeness that other experiments, to be reported elsewhere, show that the methylglyoxal production takes place by way of a totally different mechanism to acrolein production, and that surface reconstruction under the influence of the halogen atoms is of importance in the high-temperature region.

When we come to consider the results in the low-temperature region we find them to be quite varied. The highest oxide, WO_3, showed practically no activity for selective oxidation over the whole of the temperature range studied and only homogeneous pyrolysis was observed. Selective oxidation was, however, observed for the $WO_{2.95}$ samples, where, after a few pulses at 320°C, acrolein appeared in the products with a selectivity of about 15%. MoO_3 behaved in a very similar way to $WO_{2.95}$, and showed a selectivity of 22% at 320°C. In this respect it has already been shown that allyl iodide can be transformed into acrolein on MoO_3 at 300°C with 100% selectivity and that the selectivity decreased with temperature (*4*). In the present study much smaller amounts of the catalyst were used and the selectivity observed was thus lower, amounting to about 30%, at 300° and 22% at 320°C. The homogeneous reactions of dimerization and cyclization were thus competing more effectively than in the case of experiments described in Ref. (*4*). The samples of $WO_{2.72}$ and WO_2 produced practically no acrolein below 400°C.

In considering these results, we will turn to the reduced tungsten oxides first. There is clearly a significant difference in the behavior of $WO_{2.95}$, $WO_{2.72}$, and WO_2, and to account for it we should review those properties which could be relevant. Perhaps the most important of these is the ease of reducibility, or more strictly speaking, the ease with which these compounds can change their stoichiometry somewhat. With the compounds used at present, only $WO_{2.95}$ has an easily changed stoichiometry, a process which is accommodated by changing the density of *CS* planes in the crystals. In contrast to this, neither $WO_{2.72}$ nor WO_2 is easily oxidised or reduced, and they are best regarded as strictly stoichiometric compounds. Another important aspect is the structure of these compounds. Only $WO_{2.95}$ contains *CS* planes while $WO_{2.72}$ and WO_2 do not. However, WO_2 does in fact contain strings of edge-sharing WO_6 octahedra which are similar in some respects to those in the *CS* planes in $WO_{2.95}$, and $WO_{2.72}$ contains pairs of edge-sharing octahedra. A final property which may have some bearing on the ability of these materials to act as catalysts is their electronic structure. All of these materials are rather similar in this respect, having free electrons and a metallic conductivity.

A consideration of these facts suggests that the property of the materials which is of most importance here is the ease with which the oxides may be slightly reduced or oxidized. In the present case this is bound up with the presence of *CS* planes. We can note that chains of edge-sharing metal–oxygen octahedra in WO_2 and pairs of edge-sharing octahedra in $WO_{2.72}$ do not seem to be effective in oxygen insertion, so that the geometry of the *CS* plane seems of less importance than its role in allowing a facile change in the stoichiometry of the crystal. This is brought about either by increasing the number of *CS* planes present in the crystals by nucleating new *CS* planes in the WO_3-like matrix between those already formed, or else by extending or contracting existing *CS* planes along their lengths. In either case, the results tend to indicate that the involvement of *CS* planes in the reaction is crucial and that their role is in the reduction and oxidation of the crystal. That is, their role is dynamic rather than passive.

Turning to the results over MoO_3, we find a general pattern of agreement. MoO_3 is also selective for the insertion of oxygen. In terms of properties it is an insulator, reinforcing the view that electronic behavior is not important in the present case. It is nevertheless easily reduced at the temperatures used in the experiments, and on reduction it forms *CS* planes at a very early stage of the reaction (*12*). However, we should note that the geometry of these *CS* planes is different than in the case of reduced WO_3, which again supports the hypothesis that it is the formation of *CS* planes that is important rather than their structure or geometry.

Let us now pass to the discussion of the behavior of WO_3. In spite of the fact that WO_3 is known to form *CS* planes, this oxide showed practically no activity in selective oxidation in the whole low-temperature range and only homogeneous pyrolysis was observed. At first sight this result is surprising, as it is known that reduction of WO_3 in vacuum leads, in the first instance, to the formation of {102} *CS* planes of exactly the same sort as in $WO_{2.95}$. However, in other experiments (*11*) it has been found that the reduction of WO_3 crystals in a vacuum ceases below about 450°C, and heating crystals of WO_3 together with tungsten metal in sealed tubes at temperatures of up to 400°C for periods of time of up to 6 months does not reduce the WO_3 crystals by any significant degree and no *CS* planes form. It is certainly true that in the catalysis experiments we may have fiercer reducing conditions due to the presence of organic molecules or hydrogen, but as the heating times are so short we would expect no reduction of the WO_3 to *CS* plane-containing crystals. This result also has a bearing on our previous comments, as it indicates that the WO_3-like matrix in $WO_{2.95}$ will also be ineffective in oxygen insertion.

This difference between WO_3 and $WO_{2.95}$ is quite important. In WO_3, we cannot nucleate *CS* planes at the temperature of the experiment and no acrolein is produced. In $WO_{2.95}$ we will also not be able to nucleate *CS* planes, but the compound does oxidize and reduce, and also produces acrolein. The only other mechanism for the oxidation and reduction is by way of the growth or shrinking of existing *CS* planes, and this process must therefore take place during the incorporation of oxygen into the organic molecule. We thus conclude that it is not the *CS* plane as a geometrical entity which is important in the catalytic process, but rather the transformation of a corner-linked to an edge-linked arrangement of metal–oxygen octahedra which provides a route for the insertion of lattice oxygen into the hydrocarbon molecules.

Other studies make this quite reasonable. The terminations of *CS* planes can be regarded as dislocation loops, and as such are regions of very high elastic strain energy (*13*). It is this elastic strain energy which accounts for the high chemical reactivity of dislocations and probably accounts for the enhanced reactivity of the *CS* plane terminations in oxidation and reduction. Indeed, this strain energy at the *CS* plane terminations is also one of the reasons why *CS* planes will not nucleate in WO_3 at temperatures below about 450°C, as *CS* plane nucleation will involve the lattice in considerable strain.

Taking the idea that it is the change of the linkage of the metal–oxygen polyhedra at *CS* plane terminations that is of central importance in the insertion of oxygen into organic molecules, a number of other experiments were carried out to attempt to confirm it in a little more detail. The first of these was to check the involvement of iodine in the reaction, as this element should not interfere with the corner-to-edge-sharing mechanism in any way; iodine–tungsten oxides are unknown. To do this, catalytic experiments with WO_3 and MoO_3 at 320°C were carried out using allyl oxalate. Decomposition of the latter is known (*14*) to be a clean source of allyl radicals, CO_2 being formed as the only other product. Results of the experiments are summarized in Table 1 and indicate that the presence of iodine has practically no effect on the ability of the catalyst to insert oxygen at lower temperatures, corresponding to the highest selectivity of the formation of acrolein.

The facility of the removal of surface oxygen atoms, created by the *CS* transformation, should be reflected in the adsorption–desorption properties toward oxygen-containing molecules linked to the surface through their oxygen atoms. As indicated by infrared spectra (*15*), acrolein is adsorbed at the surface of molybdates and MoO_3 through its oxygen atom, which completes the coordination of the surface cation by occupying a site normally taken by surface oxygen. A similar situation can be assumed to exist at the surface of WO_3. Thus, adsorption of acrolein on WO_3 and MoO_3 at 320°C was measured by the pulse chromatographic technique. The results which are shown in Fig. 3 indicate that the amount of acrolein adsorbed on WO_3 is one order of magnitude greater than that adsorbed on MoO_3. This is consistent with our earlier comments on the ease with which the two oxides may be slightly reduced or oxidized. Thus, acrolein formed on oxidation of allyl

TABLE 1

Yield of Different Products (%) on Reacting Allyl Iodide and Allyl Oxalate at 320°C with MoO_3 and WO_3

Product	MoO_3		WO_3	
	Iodide	Oxalate	Iodide	Oxalate
C_3H_6	6.8	2.0	23.5	12.0
1.5-Hexadiene	Trace	Trace	Trace	12.0
Acrolein	76.4	68.0	Trace	3.0
Acetone	1.0	4.0	Trace	2.0
Benzene	4.1	6.0	0.2	15.4

TABLE 2

Yield of Different Products (%) on Reacting WO_3 with C_3H_5I and then $C_3H_5I + O_2$

Reactants	Yield (%)			
	C_3H_6	C_6H_{10}	C_6H_6	Acrolein
C_3H_5I (after 20 pulses)	35.5	0.5	0.6	0.8
$C_3H_5I + O_2$	9.4	Trace	Trace	36.0

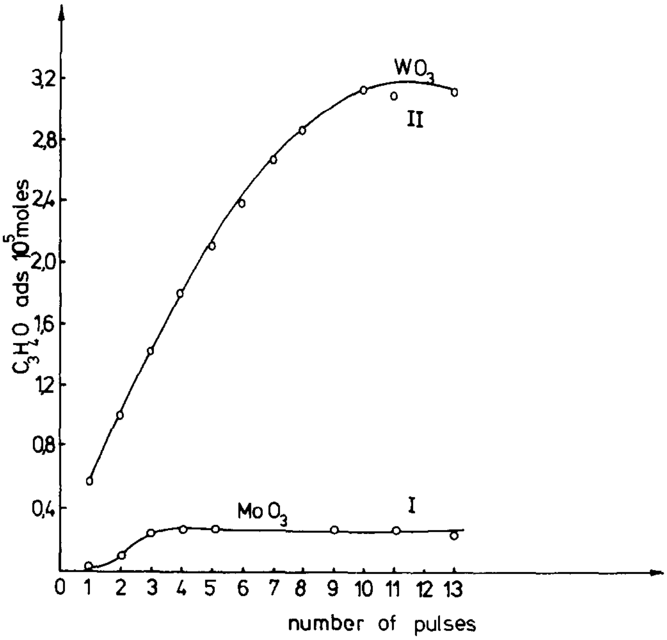


FIG. 3. Adsorption of acrolein on WO_3 and MoO_3 at 320°C.

species at the surface of MoO_3 can be fairly easily desorbed whereas any that might be formed at the surface of WO_3 is retained much more strongly and might poison or block any active centers.

It also seemed interesting to check whether the strongly adsorbed acrolein formed at the surface in the course of the reaction could be displaced by oxygen, which could adsorb on tungsten ions adjacent to the adsorbate and then fill the sites left by the desorbing acrolein. Table 2 shows the results of an experiment in which a sample of WO_3 was at first exposed to 20 pulses of allyl iodide (yields to different products observed in the 20th pulse are given in the first row) and then a pulse of $C_3H_5I + O_2$ was introduced (second row). It may be seen that even after 20 pulses of allyl iodide only about 37% of the products formed leave the catalyst bed, and less than 1% are oxygenated products. When, however, the $C_3H_5I + O_2$ mixture is introduced, acrolein becomes the main product desorbing from the catalyst. It may be thus concluded that the surface of WO_3 has some small ability to insert oxygen at low temperature into the allyl species, but desorption of the oxygenated product accompanied by the transformation from the corner-linked into edge-linked arrangement of, tungsten–oxygen octahedra cannot take place. This agrees with our findings concerning the reduction of WO_3 described above.

Further light is shed on this process when we note that the desorption of oxygenated products takes place very easily in the case of $WO_{2.95}$, which differs from WO_3 only in that it has been slightly reduced and *CS* structures have been already formed. We have already stated that the WO_3-like matrix in $WO_{2.95}$ will not support the growth of new *CS* planes and once again the evidence supports the fact that it is the *CS* planes which are already in existence which are important in this process. Moreover, as we are removing oxygen from the lattice in the desorption process, we must increase the *CS* plane length somewhat, which is in agreement with the suggestion that it is the dynamic growth and shrinkage of *CS* planes which is of importance.

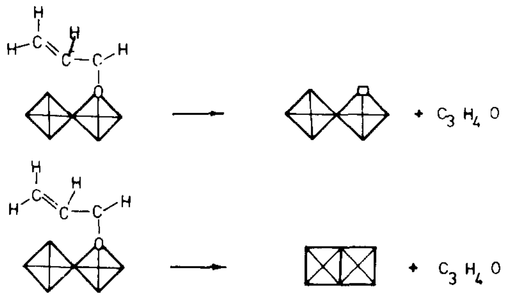


FIG. 4. Schematic mechanism for the insertion of oxygen into a hydrocarbon molecule. In (a) the formation of an oxygenated species leaves the surface of the material, shown as two corner-linked MO_6 octahedra, with a terminal oxygen atom missing. In (b) a *CS* type rearrangement of these octahedra ensures that the metal atoms preserve their normal octahedral disposition of oxygen neighbors, and no "vacancy" need be formed.

The conclusion to be drawn from all of the experiments described in this paper is that it is the ability of the molybdenum and tungsten oxides to rearrange their coordination polyhedra, manifested in the appearance of *CS* structures, which plays an important role in the catalytic insertion of oxygen into organic molecules. This mechanism is shown schematically in Fig. 4. It is quite different from that which occurs for non-*CS*-forming oxides, where desorption of the oxygenated product must result in the generation of an oxygen vacancy. This is an energetically expensive process which the *CS* mechanism avoids. Indeed, the *CS* rearrangement ensures that each cation retains its preferred nearest neighbor coordination polyhedron while allowing oxygen to be abstracted from the structure. In this sense it is therefore analogous to the role of dislocations in deformation mechanics. A dislocation allows a material to slip or deform without the necessity of bond breaking, thus making an energetically unfavorable process possible for much lower energy outlay. Similarly the *CS* operation allows the energetically costly oxygen abstraction to take place without changing the total number of nearest-neighbor M–O bonds, thus making it possible at lower temperatures and with a relatively small energy involvement.

REFERENCES

1. Haber, J., and Grzybowska, B., *J. Catal.* **28,** 489 (1973).
2. Haber, J., *Z. Chem.* **13,** 241 (1973).
3. Haber, J., *Pure Appl. Chem.* **50,** 923 (1978).
4. Grzybowska, B., Haber, J., and Janas, J., *J. Catal.* **49,** 150 (1977).
5. Haber, J., Marczewski, W., Stoch, J., and Ungier, L., *Ber. Bunsenges. Phys. Chem.* **79,** 970 (1975).
6. Stone, F. S., *J. Solid State Chem.* **12,** 271 (1975).
7. de Rossi, S., Iguchi, E., Schiavello, M., and Tilley, R. J. D., *Z. Phys. Chem. NF* **103,** 193 (1976).
8. Schiavello, M., Pepe, F., Cannizzaro, M., de Rossi, S., and Tilley, R. J. D., *Z. Phys. Chem. NF* **106,** 45 (1977).
9. Pickering, R., and Tilley, R. J. D., *J. Solid State Chem.* **16,** 247 (1976).
10. Tilley, R. J. D., *Chem. Scripta* **14,** 147 (1978–9).
11. Booth, J., Ekström, T., Iguchi, E., and Tilley, R. J. D., *J. Solid State Chem.* **41,** 293 (1982).
12. Bursill, L. A., *Proc. Roy. Soc. London* **A311,** 267 (1969).
13. Anderson, J. S., and Hyde, B. G., *J. Phys. Chem. Solids* **28,** 1393 (1967).
14. Louw, R., *Rec. Trav. Chim.* **90,** 469 (1971).
15. Grabowski, R., Haber, J., and Sloczynski, J., *Reaction Kinet. Catal. Lett.* (in press).