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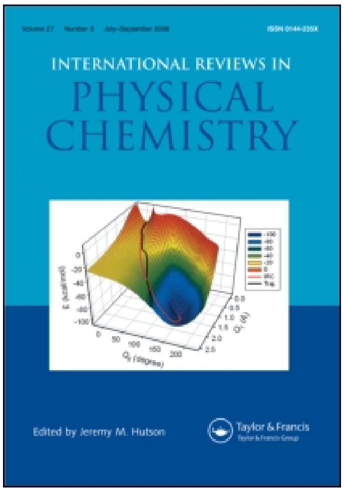

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Selectivity of Partial Hydrocarbon Oxidation

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SELECTIVITY OF PARTIAL HYDROCARBON OXIDATION

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ABSTRACT

This review of the selectivity of catalysts in the partial oxidation of hydrocarbons principally embraces those papers published from 1977 to 1982. Partial oxidation is shown to occur by the redox mechanism involving the structural oxygen of the solid oxide catalyst. The hydrocarbon molecule interacts with the oxide surface to form a relatively weakly bound allylic, or some other, dehydrogenated complex. The weakly bound hydrocarbon diffuses towards the active site where it reacts with the structural oxygen. The oxygen diffuses to the active site through the solid catalyst.

The highest activity is displayed by polyphasic multicomponent catalysts, the different phases accelerating individual stages of catalysis with possible diffusion of intermediates from one phase (one group of active sites) to the other. Non-equilibrium phases can be stabilized during catalysis; and a crystallo-chemical conformity between the constituents of the complex catalyst phases is essential for stabilization.

INTRODUCTION

One of the most important characteristics of any catalytic process is its selectivity—the suppression of undesired side reactions with consequent increase in the rate of initial conversion of reactants to the desired product. Selectivity is the determining factor in the effectiveness of a process. Its role has now greatly increased since the higher cost of petrochemicals makes it particularly vital for a most exhaustive use of hydrocarbons. An increase in selectivity is also important from the ecological viewpoint as it diminishes the hazardous exhausts and the amount of consequential waste water. We therefore see that a most important aim in catalysis is the creation of highly active and selective agents for diverse processes, in particular for partial oxidation of unsaturated and aromatic hydrocarbons.

Table 1 lists certain results obtained for the conversion and selectivity of various partial oxidation processes over modern catalysts.

A high selectivity with almost complete conversion of hydrocarbons has been attained only recently by the use of a multicomponent catalyst, or a silver catalyst modified by various additives, as in the oxidation of ethylene to ethylene oxide. *Figure 1* is a scheme of the catalyst selectivity in the oxidation of propylene to acrolein, as reported by the Heterogeneous Catalysis Department of the USSR Academy of Sciences (*see*, for example, Polotnyuk *et al.*, 1981; Krylov, 1983). In the 1950s the best catalyst was thought to be cuprous oxide with maximal selectivity 50%; in the 1960s, bismuth molybdate (selectivity 85%, conversion 82%); whereas

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TABLE 1. Selectivity of certain partial oxidation products

Catalyst	Reactant	Product	Conversion	Selectivity	References
Bi-Mo-Co-Fe-K	Propylene	Acrolein	97	92	Cullis and Hucknall (1982)
Bi-Mo-Co-Fe-Sb-K	Butylene	Methylacrolein	98	86	Cullis and Hucknall (1982)
Bi-Mo-Fe-Co-Ni-P	Propylene	Acrylonitrile	96	83	Cullis and Hucknall (1982)
V-Ti-P-rare-earth element	*o*-xylene	Phthalic anhydride	100	76-78	Polotnyuk *et al.* (1981)
V-Mo-Ni-rare-earth element	Benzene	Maleic anhydride	100	75	Polotnyuk *et al.* (1981)

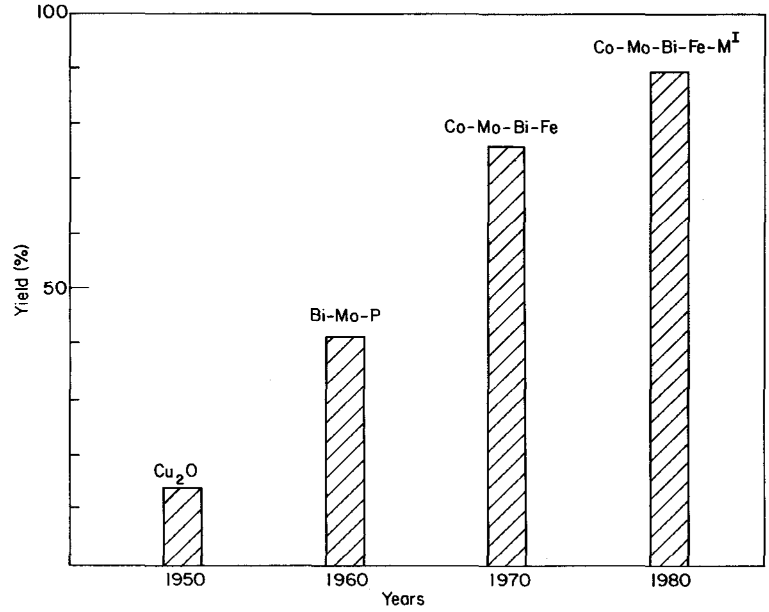


FIG. 1. Schematic illustration of the percentage of changes in yields of acrolein and acrylic acid on various catalysts, and of the changing nature of selective oxidation catalysts over the years.

four-, five- and six-component catalysts are used at present. The origin of the much higher selectivity and conversion attained with such catalysts is not quite clear and the reasons reported not obvious.

The mechanisms of partial oxidation of different hydrocarbon structures and the effect of active catalyst surfaces must be defined in order to obtain the best active and selective partial oxidation catalysts. This has been repeatedly discussed (*see* Margolis, 1977; Sleight, 1980; Grasselli and Burrington, 1981).

Certain general features of the hydrocarbon oxidation mechanism for various reactions and types of catalysts have been found:

1. The interactions of hydrocarbons with catalyst surfaces are accompanied by chemisorption of two kinds—one weakly reversible at the given temperature, and the other stable, irreversible, and often removed by oxygen only. The heat of adsorption changes with increasing coverage over the range from 50 to 200 kJ/mole. The adsorption ratio depends on molecular structure and the catalyst surface nature.
2. Whereas complete oxidation of hydrocarbons is ensured by weakly bound mobile oxygen, partial oxidation almost always requires relatively stable oxygen present in the oxide catalyst lattice.
3. The interaction of hydrocarbons with oxygen species on the catalyst surface yields compounds of different structures and oxygen bond energies. These compounds may be intermediates sustaining the partial and complete oxidation processes. Certain systems involve hydrocarbon and peroxy radicals that can either convert on the catalyst surface, or desorb to the gas phase and react there by the usual homogeneous path.
4. The redox mechanism—reduction of surface with hydrocarbon and its reoxidation with gaseous oxygen is the one most often encountered.
5. The studies on reaction mechanisms are closely connected with those on the selectivity principles in partial catalytic oxidation. Golodets (1978) found that the catalyst activity and selectivity correlate with the oxygen bond energy in the oxide and with the acid-base properties of the hydrocarbon and the catalyst surface. The most selective oxides are those of Mo, V, Nb and Ti. This is thought to depend both on the oxygen bond strength in oxides and on the acidic properties of the latter.

1. SURFACE HYDROCARBON COMPOUNDS

As found from the electroconductivities and work functions of all the oxide catalysts studied, olefin adsorption results in a negative charge of the surface, i.e., the adsorbed olefins are electron donors. However, the basic information about hydrocarbon adsorption on oxides has been obtained by means of UV spectroscopy.

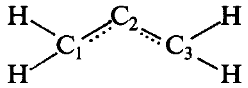
Table 2 lists the basic surface compounds formed in hydrocarbon adsorption, as obtained by UV spectroscopy for various oxidation reactions.

TABLE 2. Characteristic surface compounds in hydrocarbon oxidation

Hydrocarbon	Catalyst	Surface compounds	References
Ethylene	Ag	$\dot{C}H_2\text{-}CH_2\text{-}O\text{-}Ag$ $CH_3\text{-}\dot{C}H\text{-}O\text{-}Ag$ $\underset{\substack{\downarrow \\ Ag}}{CH_2=CH_2}$	Force and Bell (1975)
Propylene	MoO_3/MgO	$CH_3\text{-}CH=CH_2$ π-complex	Davydov *et al.* (1978)
	V_2O_5/MgO		Kadushin (1979)
	Cu-O/MgO		Morozova (1981)
	Bi-MoPO/MgO	$CH_2=CH\text{-}CH_3$ π-, δ-complex	
Butylene	ZnO	$CH_3\text{-}CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2$	Ono and Kobokawa (1978)

Ethylene forms relatively weak π-complexes with metal cations (M) on the surface of oxide $\underset{\mathrm{M}}{\underset{\downarrow}{\mathrm{C}{=}\mathrm{C}}}$ with an adsorption heat of 30 to 60 kJ/mole. Their formation is seen from the decreasing multiplicity of the C = C bond. The stretching vibration frequency of the C = C bond in π-complexes is 30–80 cm^{-1} lower compared to that in gaseous ethylene (1621 cm^{-1}) (Krylov and Kiselev, 1981).

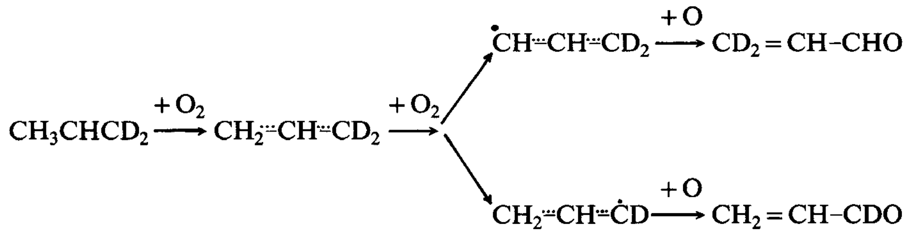
Alongside the π-complexes, propylene adsorption also yields a π-allyl complex



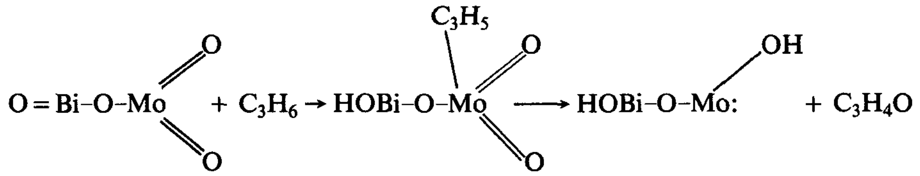
According to various results (Kadushin, 1979) the stretching vibration frequency ν of the C–C bond shifts by 100–150 cm^{-1} compared to that for free propylene. Other bands appear simultaneously near 3660 cm^{-1} of the O–H bond stretching vibration region. These are due to detachment of the H atom from propylene ($C_3H_6 \rightarrow C_3H_5 + H$) and the formation of O–H groups on the surface. Asymmetric δ-allyl complexes $CH_2{=}CHCH_2{-}M$ or $CH_2{=}CH{-}CH_2{-}O{-}M$ had also been found (Efremov *et al.*, 1979; Kadushin, 1979). Certain recent data (Higatsune, 1982) obtained from the UV spectra of propylene complexes with individual metal atoms in the matrix highlight the problem of a different interpretation of propylene spectra on oxides assigned previously to π-allyl.

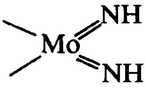
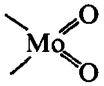
The formation of π-allyl complexes during propylene adsorption on oxides was inferred from catalysis data much earlier than the UV spectra of adsorbed propylene were obtained.

It follows from the reported results (Adams and Jannings, 1963, 1964) that the first oxidation step of propylene (deuterated in the extreme position) on Cu_2O is the hydrogen atom detachment from the olefin methyl group to form a symmetric π-allyl. The second hydrogen atom detaches with equal probability from the first (C_1) or the third (C_3) olefin atom to form the partial oxidation product—acrolein:



The same results were obtained for ^{14}C-labelled propylene oxidation. When C_3H_6 was oxidized on bismuth molybdate, both C_1 and C_3 displayed similar properties and were converted to an intermediate complex at the same rate (Voge *et al.*, 1963). The step of intermediate π-allyl generation was suggested to be rate-determining. Others believe that, alongside the hydrogen atom detachment from the olefin molecule, there occurs interaction with oxygen to form a hydroperoxide allyl $CH_2{=}CH{-}CH_2OOH$ further converting to oxygen-containing products (Margolis, 1963; Daniel and Keulks, 1971). Certain authors (Burrington and Grasselli, 1979; Burrington *et al.*, 1980) claim that propylene is chemisorbed on active sites of the catalyst surface yielding an allyl radical that attacks oxygen to form acrolein



In the presence of ammonia a complex  is formed instead of , followed by acrylonitrile. Such a scheme fits both the kinetics (first order in olefin) and the value of the kinetic isotope effect.

The π-allyl radical seems to form by the redox mechanism. The UV spectra show that π-allyl complexes are readily formed on catalysts of the base type (Bi_2O_3, CoO, MgO, etc.). The C–H bonds in such complexes will be weaker due to redistribution of the excess charge through the antibonding orbital

$$C_3H_6 + O^{2-} \rightarrow C_3H_5^- + OH^-$$

Virtually at the same time $C_3H_5^-$ seems to interact with the metal in its highest valence state

$$C_3H_5 + M^{(n+1)+} \rightarrow C_3H_5M^{n+}$$

The C_3H_5 charge in the complex so formed is thought to be close to zero and its reactivity must be high.

The allyl radical desorption in propylene oxidation on MnO_2 was found by mass-spectrometry (Hart and Friedli, 1970). The π-allyl radicals were first found by the EPR technique in the presence of selective catalysts for oxidation of propylene to acrolein (various phases of bismuth molybdate) (Marte and Lunsford, 1981). With a small amount of oxygen in the reactant mixture the radicals convert to peroxy radicals. The activation energy for allyl radical generation is 60 kJ/mole.

Oxidized surface olefin species were observed alongside the strictly hydrocarbon structures. Strong interaction of the olefin with the surface results in its breaking into fragments at the double bond and to subsequent oxidation of these fragments to carbonate and carboxyl complexes. A molecule of ethylene yields two formate ions $HCOO^-$: that of propylene gives acetate CH_3COO^- and formate, that of butylene—1-propionate $C_2H_5COO^-$ and formate etc. Subsequently these structures convert to the products of complete oxidation—CO and H_2O.

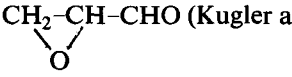
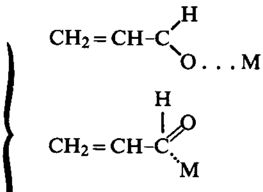
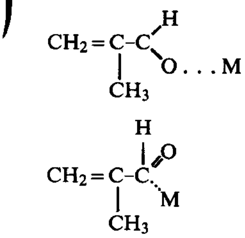
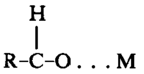
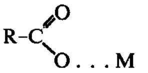
Less oxidized structures have also been found: carbonyl compounds (Morozova, 1981) and glycide aldehyde  $CH_2\text{–}CH\text{–}CHO$ (Kugler and Gryder, 1976). These can be conceived as intermediates in catalysis. *Table 3* lists the results for the structures of the oxygen-containing products of hydrocarbon oxidation, observed on surfaces of partial oxidation catalysts. To determine their contribution to catalysis, the rates of their formation and consumption have to be measured in the course of catalysis and the reaction products have to be recorded. Such spectrokinetic methods permit the detection of the active catalytic species among the multiple surface compounds.

TABLE 3. Surface oxygen compounds

Adsorbed species	Catalyst	Surface compounds	References
Acrolein	$CoMoO_4 + V_2O_5$		Morozova (1981) Kadushin *et al.* (1981)
Methylacrolein	V_2O_5-MoO_3		
Isobutyric, propionic and crotonic aldehyde	$CoMoO_4 + V_2O_5$	 $R{-}\overset{H}{\overset{\vert}{C}}{-}O\ldots M$	
Acrylic and methacrylic acid			

Consequently the diverse schemes proposed and often based on occurrence of many possible chemical reactions are of little use unless the true process-carrying intermediate is determined and the rates of its formation and conversion are found and compared with those of the overall reaction.

The formation and consumption of a π-allyl complex in propylene oxidation on a MgO-supported bismuth molybdate were studied in a special flow cell—a catalytic reactor (Kadushin *et al.*, 1981). However, partial oxidation products were not found under these conditions.

Isobutylene oxidation on a multicomponent active Mg-Mo-Bi-Fe-O partial oxidation catalyst was studied in the course of catalysis in a flow reactor, recording the products by a Fourier transform IR spectrometer (Krylov, 1982). No surface allyl was observed, but there was a strongly oxidized complex of the methacrylic anhydride type that represents a precursor for methacrolein formation. On a catalyst with specific surface 5 m^2g^{-1} this complex occupies less than 1% of the surface.

Spectroscopic data on the structures of surface species formed by adsorption of aromatic hydrocarbons on selective catalyst surfaces are virtually absent from the scientific literature. However, a rather detailed scheme involving intermediates and radicals has been reported by Germain (1972) and is shown in *Figure 2*. But not all the intermediates given in the scheme have been identified. Consequently, it would be premature to consider that the mechanisms of certain oxidation reactions of this class of organic compounds have been elucidated.

As shown by spectroscopy, carbonate and carboxyl structures appear on

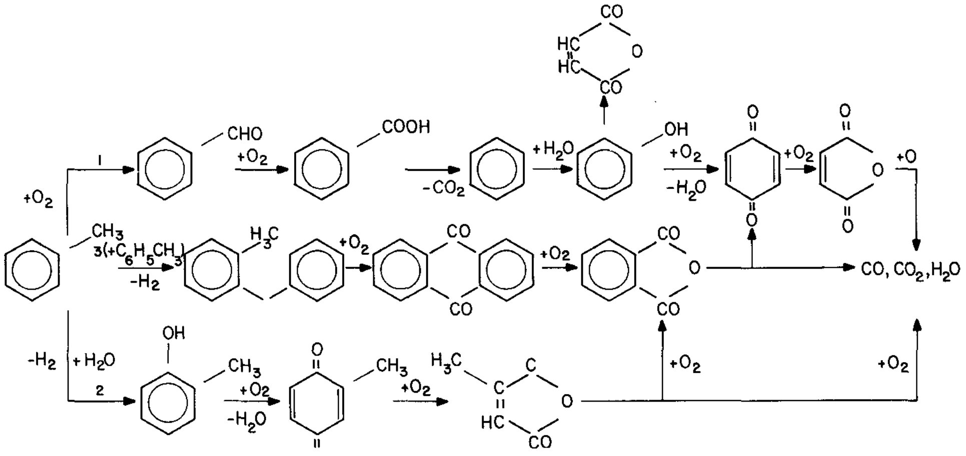


FIG. 2. Scheme of toluene oxidation (Germain, 1972).

adsorption of saturated hydrocarbons (Sokolovskii *et al.*, 1974). On many oxide systems these species oxidize only to CO_2 and H_2O. Evidence of the formation of peroxy radicals of the type R–CO–O–O–CO–R′ has also been reported (Ukharskii *et al.*, 1980).

Thus analysis of the available data on the nature of surface species formed by interaction of the oxidizing organic molecules with surfaces of various catalysts reveals how difficult it is to control the selectivity of oxidation processes. There is almost no information about the participation of these species in the generation of end products in the partial oxidation of valuable oxygenated hydrocarbons.

2. STATE OF OXYGEN AND THE CATALYST STRUCTURE

Germain (1972) considers that the ability of catalyst cations to π-bond the reacting organic molecules (complexing) is an important factor in governing selectivity. The strength of cation bonds with such molecules seems to be more important than the mobility and energy of oxygen bonds. Yet, others consider that the state of oxygen and the catalyst structure are more important selectivity factors than the nature of surface species arising from the interaction of organic molecules and catalysts (Keulks *et al.*, 1978; Grasselli *et al.*, 1981). Most researchers consider that the interaction of an organic compound with the metal ion and the lattice oxygen (for instance formation of an allyl complex) is the rate-limiting step in the conjugated redox process of partial oxidation. Opposing points of view have, however, also been reported (Keulks *et al.*, 1978; Grasselli *et al.*, 1981).

Oxygen is readily chemisorbed on almost all oxide catalysts, forming molecular and atomic radical ions such as O_2^- and O^- and other species. Moreover, there is the catalyst lattice oxygen bound in the catalyst structure with various bond energies, depending on the cation valence state and on the given solid structure. The chemisorbed oxygen species can be assimilated into the oxide by the familiar scheme

$$O_2\,(\text{gas}) \rightarrow O_2\,(\text{ads}) \xrightarrow{e} O_2^- \xrightarrow{e} 2O^- \xrightarrow{2e} 2O^{2-}_{\text{latt}}$$

This succession of O_2 conversions is widely accepted (*see*, for example, the reviews by Hucknall (1974) and Cullis and Hucknall (1982). It will be noted, however, that the involvement of O_2^- and O^- ions in further interaction with the lattice electrons has only a small probability. The formation of covalent oxygen species would be more probable. On many oxides the radical ions O_2^- and O^- form independently at different sites: O_2^- at the site transmitting one electron, and O^- on that transmitting two electrons (Spiridonov and Krylov, 1975).

Since the catalyst selectivity in partial oxidation is usually ascribed to lattice oxygen O^{2-}, many researchers (e.g., Boreskov, 1964) compared the rates of hydrogen removal from the lattice with those of heteromolecular exchange between the lattice and the gas phase oxygen

$$M_n{}^{16}O_m + {}^{18}O_2 \rightarrow M_n{}^{16}O_{m-1}{}^{18}O + {}^{16}O\,{}^{18}O$$

The reactivity and mobility of lattice oxygen can be estimated from the heteroexchange rate. *Table 4* lists relevant data for typical oxidation catalysts. The lattice oxygen mobility (exchange rate) changes by several powers of ten, and the activation energies differ by 50–80 kJ/mole depending on the catalyst type. However the bond energies and mobility of the lattice catalyst can change considerably even on the same catalyst specimen, if the catalyst is partially reduced. The removal of a 16% oxygen monolayer on bismuth molybdate increases the oxygen bond energies in the lattice from 254 to 350 kJ/mole (Margolis, 1977).

Consider the specific features of selective catalyst structures responsible for the catalyst mobility. Take the most extensively studied bismuth molybdates. Detailed information on the structures of three bismuth molybdate phases can be found in the review by Keulks *et al.* (1978). They differ in M–O bond length and the number of oxygen ions surrounded by molybdenum and bismuth ions, and also in the location of octahedra and terahedra containing Mo and Bi ions.

The α-phase ($Bi_2O_3 \cdot 3MoO_3 \rightarrow Bi_2Mo_3O_{12}$), the β-phase ($Bi_2O_3 \cdot 2MoO_3 \rightarrow Bi_2Mo_2O_9$) and the γ-phase ($Bi_2O_3 \cdot MoO_3 \rightarrow Bi_2MoO_6$) are distinguished. The first corresponds to the defect scheelite structure ($CaWO_4$) and can formally be written as $Bi_{2/3} \square_{1/3} MoO_4$, where $\square$ denotes ordered cation vacancies, Mo is in tetrahedral coordination, and the coordination number of Bi is 8. In the orthorhombic β-phase the coordination numbers of Mo are 4 and 6. The stoichiometric γ-phase crystallizes in the orthorhombic lamellar lattice of koechlinite where Mo is in sixfold coordination. This structure can be represented as an alternating entity of $(BiO^+)_{2n}$ and

TABLE 4. Oxygen heteroexchange on certain oxide catalysts

Catalyst	Exchange rate at 600°C m^{2}sec	Activation energy kJ/mole	References
V_2O_5	1.3×10^5	196	Boreskov (1964)
MoO_3	1.0×10^5	130	Boreskov (1964)
Sb_2O_4	1.4×10^9	213	Boreskov (1964)
Bi_2O_3	1.0×10^8	188	Panov (1971)
$CoMoO_4$	2.1×10^7	175	Panov (1971)
$Fe_2(MoO_4)_3$	5×10^5	200	Panov (1971)
$V_2O_5 + MoO_3$ (33%)	1.7×10^5	196	Blanchard (1972)
$V_2O_5 + TiO_2$ (40%)	7×10^4	200	Blanchard (1972)
$Sb_2O_4 + Fe_2O_3$ (50%)	9×10^{10}	146	Muzykantov *et al.* (1969)

$(MoO_4^{2-})_n$ layers. The Mo layer represents distorted octahedra connected at four apexes with each other, and at two—with the Bi layer. The Bi coordination is also octahedral.

Most attention was paid to the γ-phase. The lamellar structure of koechlinite and its defects that can be regulated by addition of certain (e.g. alkali) ions have been suggested (Schuit, 1974) to favour oxygen diffusion over the lattice, and to promote the selectivity of hydrocarbon oxidation. The oxygen atoms are believed to migrate to the γ-phase surface between the Bi and Mo layers.

The surface structures of active bismuth molybdate phases have been studied by UV and Raman spectroscopy techniques (Matsuura, 1980). The $Bi_2Mo_3O_{12}$ catalyst spectra exhibited two sets of bands, one resembling the bands of the Bi_2MoO_6 γ-phase, and the other those of the β-phase. The Bi_2MoO_6 phase was found to contain defects due to irregular distribution of molybdenum and bismuth ions in the structure. The absence of cation vacancies in the lattice prevents the migration of defects, but if excess molybdenum is added to this phase, this induces rearrangement of the koechlinite

$$Bi_2MoO_6 \xrightarrow{+Mo} (Bi_{1.57}\,Mo_{0.287}\,\square_{0.143})\,(Mo_{0.857}\,Bi_{0.143})O_6$$

The β-phase of $Bi_2Mo_2O_9$ arises on the catalyst surface. Its structure is a combination of scheelite (α-phase) and koechlinite (γ-phase). In the scheelite structure four Mo ions are bound in a cluster Mo_4O_{16}. The clusters are bound with each other by bismuth atoms. The Bi atoms are positioned on the axis passing through the centres of Mo_4O_{16} squares. The koechlinite structure contains similar elements (Mo_4O_{16})–Bi–(Mo_4O_{16}) bridged by oxygen between the Bi cations.

These concepts are consistent with the suggestion (Sleight and Linn, 1976; Sleight, 1980) that a necessary condition of the active site formation is the presence of cation vacancies (absence of Bi^{3+}) $Bi^{I}(Bi^{II}\,\square\,O_2)\,(Mo_4O_{16})$. Here Bi^{I} and Bi^{II} denote Bi atoms in different coordination. If Bi^{I} migrates towards the cation vacancy □, the structure will be $\square^{I}(Bi_4^{II}O_2)\,(Mo_4O_{16})$.

The lamellar structures also involve vanadium pentoxide, vanadium–molybdenum, vanadium–phosphorus, and vanadium–titanium oxide systems that are active in the oxidation of aromatic hydrocarbons. Oxygen diffusion in these systems is facile. Kofsted (1972) noted that the V_2O_5 structure contains tunnels aligned parallel to the (001) and (010) directions and large enough to permit entry of an O_2 molecule. Though many results obtained by comparison of the catalysis and reduction rates are available, the data about re-oxidation rates are few and there are virtually no quantitative estimates of oxygen diffusion through various systems, particularly during catalysis.

Table 5 lists the oxygen diffusion coefficients in various oxide systems at temperatures markedly higher than that for hydrocarbon oxidation. These can differ by many orders, but comparison, for instance, of a stoichiometric zirconium oxide with a sample exhibiting a decreased number of oxygen ions shows an increase of three orders, due to formation of anionic vacancies in the oxide. The specific features of vanadium bronze structures (tunnels between ion layers) cause a several hundredfold decrease in the temperature of initial oxygen diffusion over the lattice, and a higher diffusion coefficient compared to that of pure vanadium oxide ((V_2O_5) (Volkov and Novak, 1980). It will also be noted that in disperse powders, i.e., in the usual form of oxide catalysts, the diffusion coefficient is much lower than in monocrystals. For instance, in single crystals of $CaWO_4$ and $CaMoO_4$ the diffusion

TABLE 5. Oxygen diffusion in oxide systems

Solid	Temperature °C	Diffusion coefficient cm^2/sec	Activation energy kJ/mole	References
TiO_2	1000	10^{-14}	165	Kofsted (1972)
UO_2	500	10^{-12}	120	Kofsted (1972)
Nonstoichiom.ZrO_2	875–1050	10^{-5}*	128	Kofsted (1972)
Co_3O_4	900	10^{-9}	–	Tretyakov (1978)
V_2O_5		10^{-8}	103	Volkov and Novak (1980)
$M_xV_2O_5$ (bronze)	400–700	10^{-6}	115	Volkov and Novak (1980)

*Stoichiometric ZrO_2 $D = 10^{-8}$

coefficients are five orders of magnitude lower than in polycrystalline powders of the same composition (Tretyakov, 1978).

In the sub-surface layer the diffusion coefficient is lower than in the bulk; hence a considerable number of layers of the catalyst become involved in oxidation and reduction processes on oxide catalyst surfaces (Kofsted, 1972; Tretyakov, 1978; Volkov and Novak, 1980).

The reduction of many oxides representing partial oxidation catalysts yields the so-called crystallographic shear structures. For instance MoO_3 consists of disrupted MoO_6 octahedra connected by their apexes. Reduction causes oxygen detachment from the structure, a vacancy is formed, these vacancies condense and, in due course, the separation of Mo atoms becomes smaller and the octahedra are then connected through edges, with the preservation of octahedral coordination (*see* Anderson, 1972).

In terms of this mechanism MoO_3 yields oxides of composition Mo_nO_{3n-x}, where x is a small number (1, 2, 3 . . .) and n can be high. For instance oxides of composition Mo_8O_{23}, Mo_9O_{26}, $Mo_{10}O_{29}$, $Mo_{11}O_{36}$, $Mo_{18}O_{38}$ and $Mo_{29}O_{75}$ have been found (Krylov and Kiselev, 1981) and blocks of a relatively unchanging structure, divided by the shear planes, were formed. The crystallographic shear energy in such structures is small, and oxygen diffusion is easy. Faster oxygen diffusion and lattice reduction have been found for structures of the crystallographic shear of $Mo_xW_{1-x}O_3$ (Barba *et al.*, 1982).

It is recognized that structural oxygen is removed during catalysis; thus it follows that, at steady state, the vacancies formed are replenished by the oxygen in the catalyst bulk. In other words, the catalyst acts not only as a reaction component, but also as an oxygen pump. It would be natural to suggest that oxygen migration over the catalyst or in the sub-surface layers is controlled by diffusion and that its rate depends on the solid structure.

It has been found by isotope labelling that, despite the relatively high bond energies involved, many catalyst layers are implicated in the selective oxidation of propylene (both partial and complete) on various catalysts (Boreskov, 1964; Panov, 1971; Hoefs, 1978; Krenzke and Keulks, 1980a, b). Relevant results obtained using the oxygen isotope ^{18}O are given in *Table 6.*

When propylene oxidizes on the koechlinite (Bi_2MoO_6) γ-phase all the oxygen in the solid is involved in catalysis. Similar results were obtained for the most active catalyst Bi–Mo–Fe–O. On the β-phase of bismuth molybdate ($Bi_2Mo_2O_9$) not all oxygen is capable of oxidizing propylene (Hoefs, 1978).

Selective oxidation of propylene on a uranium–molybdenum catalyst occurs by

TABLE 6. The contribution of structural oxygen to propylene oxidation at 400°C

Catalyst	Selectivity (to acrolein) %	Number of oxygen layers involved in formation		Percentage of catalyst oxygen involved in formation		References
		Acrolein	CO_2	Acrolein	CO_2	
$Bi_2Mo_3O_{12}$	88	22	22	4.4	4.4	Krenzke and Keulks (1980a)
Bi_2MoO_6	92	282	282	100	100	Krenzke and Keulks (1980a)
$Bi_3FeMo_2O_{12}$	86	64	32	100	48	Krenzke and Keulks (1980b)
USb_3O_{10}	82	–	–	0.6	0.6	Hoefs *et al.* (1979)

the redox mechanism, but here the mobility of the structural oxygen is very low. The oxide catalyst contains oxygen of different kinds involved in selective and complete oxidation (Prasada Rao *et al.*, 1979). The content of such 'selective' oxygen in bismuth molybdate is 24–33%, and for iron molybdate, cobalt and nickel the values are 8, 22 and 1.5%, respectively. It is thought that the active oxygen ions O_2^- and O^- are responsible for complete oxidation, whereas the bulk oxygen is directly involved in partial oxidation, and that equilibrium is sustained between the respective species. After active oxygen is removed from the surface by interaction with the reducing agent, the catalyst activity is ensured by ingress of the bulk oxygen (Marak *et al.*, 1977).

As stated above, selective oxidation occurs by the redox mechanism

$$RH + O_{latt} \rightarrow R'O + H_2O$$

$$M_{n-1} + m/2\, O_2 \rightarrow M_nO_m$$

When the catalyst action is continuous, re-oxidation usually does not limit the oxidation processes. The kinetic data on multiple oxidation reactions of hydrocarbons of different structure (Kiperman, 1979) show that, as a rule, the rate of partial oxidation is independent of the oxygen concentration in the gas phase. The oxidation and reduction rates of certain oxide catalysts have been studied by Burrington *et al.* (1980), Brazdil *et al.* (1980), and by Grasselli and Burrington (1981) (*Table 7*).

The rates of reduction with propylene were found to decrease in the order: Multicomponent Co–Mo–Bi–Fe–O catalyst > β-Bi–molybdate > α-phase $Bi_3FeMo_2O_{12}$ > γ-phase, but the differences in reduction rates are not significant. Reduction in the presence of ammonia with these same catalysts yields acrylonitrile.

The oxidation rates of the catalysts studied differ by 2 to 3 orders of magnitude. Moreover, with increasing extents of reduction the re-oxidation rate markedly decreases (*Table 7*). At 430°C the re-oxidation rates follow the order: γ-Bi_2MoO_6 > β-$Bi_2Mo_2O_9$ > γ-$Bi_2Mo_3O_2$ > $Bi_3FeMo_2O_{12}$ > Co–Mo–Bi–Fe–O. The re-oxidation rate is proportional to $[O_2]^{1/2}$. The smallest dependence of the re-oxidation rate on the extent of reduction is observed for γ-bismuth molybdate, due to the 'linear' lattice of koechlinite. Two different regions were found for all other catalysts: one with low re-oxidation activation energies, E (5 to 30 kJ/mole), for small extents of reduction, and the other with high excitation energies (over 100 kJ/mole) for high extents of reduction.

In the ammoxidation of propylene the order of catalyst activity approximately

TABLE 7. Ratio of reduction and re-oxidation rate constants and activation energy for oxide catalyst re-oxidation

Catalyst	Reduction rate (micromoles of removed oxygen) M^{-2} at 430°C pulse $C_3H_6 + NH_2$	$K_{red}/K_{re\text{-}ox}$ 430°C	Amount of removed oxygen $10^{19}M^{-2}$	Activation energy for re-oxidation (320–460°C) kJ/mole	References
$Bi_2Mo_3O_{12}$ (α)	1.78	40.2	0.2	5.4	Brazdil *et al.* (1980)
			0.5	5.8	
			1.4	108	
$Bi_2Mo_2O_9$ (β)	1.44	57.8	0.1	34	Brazdil *et al.* (1980)
			0.3	40	
			0.8	111	
			1.5	108	
Bi_2MoO_6 (γ)	1.07	10.7	0.2	5.0	Brazdil *et al.* (1980)
			0.5	34	
			1.3	33	
$Bi_2FeMo_2O_{12}$	1.17	106.1	0.1	4.0	Brazdil *et al.* (1980)
			0.4		
			0.9		
			1.4		
$M_1^{2+}M_2^{3+}Bi_xMo_yO_z$	1.26	587.1	0.1	15	Brazdil *et al.* (1980)
			0.5	22	
			1.3	110	

coincides with that of the catalyst reduction rates. A very high ratio of re-oxidation to reduction rate constants (e.g., 587) was found for the most active multicomponent catalyst. This shows that the best selective oxidation catalyst is that capable of fast oxygen migration from the catalyst bulk to active sites, diffusion not necessarily being from the whole bulk. Active catalysts are those where the redox processes in the near-to-surface layer are readier (here the multicomponent catalysts).

The migration of oxygen over the oxide catalyst lattices depends on the catalyst structure. *Figure 3* is a schematic view of the distribution of octahedra consisting of molybdenum and oxygen ions in active catalysts for propylene ammoxidation (Sleight and Linn, 1976).

Another activity order, $Bi_2MoO_6 > Bi_2Mo_3O_{12} > Bi_3FeMo_2O_{12}$, was found for oxidation of propylene to acrolein (Krenzke and Keulks, 1980a, b). It was suggested that in the low temperature range (< 400°C, $E = 60$–75 kJ/mole) the process is limited by surface re-oxidation, and at high temperatures ($E = 170$–210 kJ/mole) by reduction and formation of the π-allyl complex. The same was found for β-$Bi_2Mo_2O_9$ (Monnier and Keulks, 1981).

Labelled catalysts such as γ-$Bi_2O_3 \cdot Mo^{18}O_3$ and γ-$Bi_2{}^{18}O_3 \cdot MoO_3$ have been prepared (Miura *et al.*, 1979) and experiments on surface reduction propylene, and propylene oxidation to acrolein using these with catalysts showed that O atoms enter acrolein from the $(BiO^+)_{2n}$ layers, and re-oxidation occurs through the $(MoO_4^{2-})_m$ layer.

The oxygen path in the bismuth molybdate structure during selective oxidation

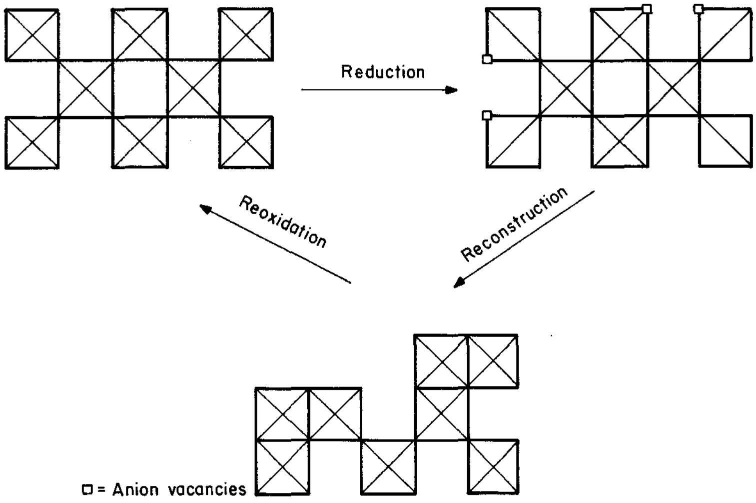


FIG. 3. Distribution scheme of molybdenum and oxygen ion octahedra in propylene ammoxidation catalysts (Burrington *et al.*, 1980).

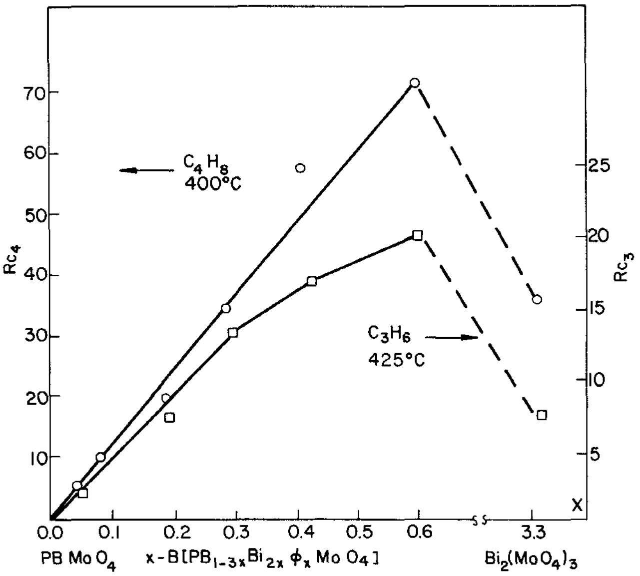


FIG. 4. Propylene and butylene oxidation rates as a function of defects in the $Pb_{1-3x}Bi_{2x}\square_xMoO_4$ catalyst (Sleight and Linn, 1976). R denotes rate [mole $h^{-1}m^{-2}$] 10^4.

has been calculated (Dadyburjor and Ruckenstein, 1978). It was suggested that the molybdate ion vacancy acts as a 'pumping relay', absorbing oxygen from the gas phase and transmitting it through the Bi–O–Mo layers. After the initial adsorption of olefin the oxygen from the bismuth ion oxidizes the surface compound so formed. The re-oxidation mechanism is not yet clear, and consequently it is, as yet, impossible to create a catalyst structure with predetermined number and nature of defects and oxygen diffusion rates. Neither is it possible to assess the selectivity of various oxidation processes from such data. But in general it can be seen that defects in the systems favour oxygen transport over the catalysts and, hence, their selectivity for catalytic oxidation.

Figure 4 presents the changes in olefin oxidation rates on the $Pb_{1-3x}Bi_{2x}\square_x(MoO_4)$ catalyst (from the data in Sleight and Linn, 1976). The oxidation rate is seen to depend on the number of defects. The maximal rate of C_3H_6 and C_4H_8 oxidation is displayed for a certain number of structural defects. The nature of these defects (whether cationic or anionic) is unknown for many systems. The number of anionic defects depends on the diffusion of oxygen, while the defects seem, in turn, to depend on the reaction rate.

3. PARTIAL OXIDATION AND SELECTIVITY MECHANISM

The nature of active sites where the oxidized molecules react with oxygen has long been discussed in papers concerned with hydrocarbon oxidation. The redox mechanism of catalysis in partial hydrocarbon oxidation was almost always accepted. The importance of oxygen bond energy with metal ions and the diffusion of oxygen through the lattice, as factors significant for the process selectivity, have been discussed above. However, there is no unanimity as to which active sites are responsible for adsorption and activation of hydrocarbons and oxygen.

At first, individual oxides—cuprous oxide, vanadium pentoxide, etc.—were used as catalysts. It was soon found, however, that anions of another valence arise in such oxides during catalysis and that the active sites involved mixed valence 'compounds'.

$$Cu^{2+} - Cu^{+};\ V^{5+} - V^{4+}, \text{etc.}$$

The more complicated composition of catalysts needed for greater activity and selectivity suggested the existence of different active sites on the catalyst surface. For instance, active contents of the bismuth molybdate surface are thought to contain molybdenum and bismuth ions, and those of the vanadium molybdenum catalyst—vanadium and molybdenum ions, etc.

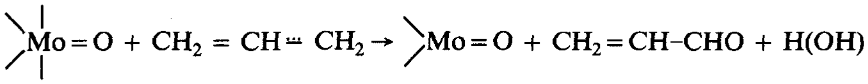
Table 8 presents the points of view of several authors as to the role of Bi and Mo atoms in partial olefin oxidation on a bismuth molybdate surface (Grasselli *et al.*, 1981). Irrespective of the different suggestions about the ions responsible for activation of molecules, almost all researchers think that the catalyst displays separate functions: the hydrocarbon is adsorbed on one ion, and oxygen enters into the reaction from the nearest ion, either of the same (e.g., Mo) or of another (e.g., Bi) chemical nature. However, most researchers claim (*see Table 8*) that, in the case of Bi molybdates, olefin chemisorption occurs on the anion-forming element, Mo. Similarly, it has been suggested that for instance with $FeSbO_4$ olefin is adsorbed near Sb (Matsuura, 1974), and with vanadates near V.

Trifiro *et al.* (1968, 1971) and Forzatti *et al.* (1978) consider that the selectivity of

TABLE 8. Active sites in bismuth molybdate (according to Burrington *et al.*, 1980)

	Matsuura *et al.* (1980)	Haber and Grzubowska (1972)	Sleight (1980)	Burrington and Grasselli (1979)
Olefin chemisorption	Mo	Bi	Mo	Mo
Allyl formation, removal of first H atom	Mo	Bi	Mo	Bi
Removal of other atoms	Mo	Mo	Mo	Mo

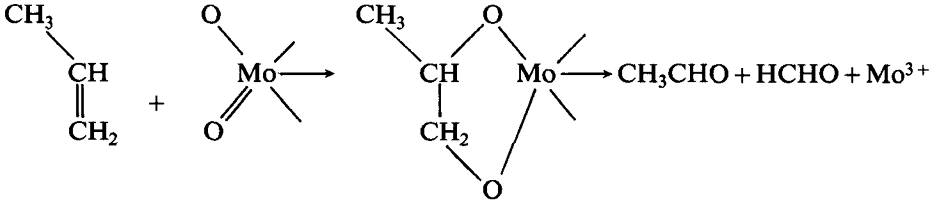
molybdate catalysts in olefin oxidation to oxygen compounds is due to the presence of a double bond $M=O$. This is supported by satisfactory correlation between selectivity of the molybdate catalysts and the 920–930 cm^{-1} UV band intensity ν_1 responsible for the $M=O$ bond in molybdates. A decrease in intensity of the ν_1 band in MoO_3/Al_2O_3 catalysts on interaction with olefin has been observed (Akimoto and Echigoya, 1973). This cannot be considered as unambiguous proof of the $M=O$ bond contribution to catalysis, since the extinction coefficients of $Mo=O$ and Mo–O bonds were not precisely measured. The interaction of olefin (or allyl) with one $M=O$ group yields an unsaturated aldehyde



$$\mathrm{>Mo{=}O + CH_2{=}CH \cdots CH_2 \rightarrow\ >Mo{=}O + CH_2{=}CH{-}CHO + H(OH)}$$

and Mo(VI) reduces to Mo(IV).

The interaction with two Mo–O bonds may result in breaking of the $C=C$ bond in olefin



and reduction of Mo(VI) to Mo(IV) (Portefaix *et al.*, 1980). However the EPR data reported show that Mo(V) is the state which is stable after reduction (Okamoto, 1981). With alcohol oxidation the redox process follows path $Mo(V) \rightleftharpoons Mo(IV)$ (Niwa *et al.*, 1981).

For V-containing catalysts the $\geqslant V=O$ bonds are similarly assumed to be involved in selective oxidation (Trifiro *et al.*, 1968). There occurs the reduction of V^{5+} to V^{4+} or V^{3+}. However, the role of $V=O$ groups in V_2O_5 and $V_2O_5 \cdot MoO_3$ in the selective oxidation of benzene to maleic anhydride has been disputed (Bielanski and Inglot, 1977). It was suggested that after reduction of the $V=O$ groups there occurs interaction with the benzene molecules to form π-complexes. As to the cation-forming element in two-component oxide catalysts, it is mostly thought to be involved in detachment of H from the hydrocarbon molecule (*see* e.g., Hucknall, 1974; Cullis and Hucknall, 1982).

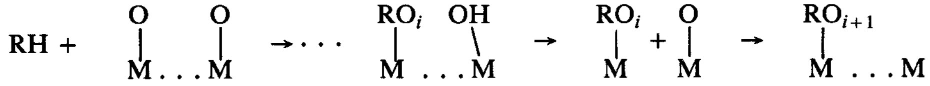
The general reasons for the oxide catalyst selectivities have been discussed by many researchers. Thus, Kiperman (1979) analyses the selectivity of oxidation reactions in terms of their development by a parallel or a consecutive mechanism. The parallel scheme seems to be more advantageous for partial oxidation, whereas, for more oxidized products, the best selectivity is obtained with a consecutive scheme, other things being equal. With a strictly parallel mechanism the selectivity S must be independent of conversion. For instance, for ethylene oxidation on chlorine-promoted silver catalysts

$$S = \frac{k_2}{k_1 + k_2}$$

where k_1 and k_2 are the rate constants of ethylene conversion to ethylene oxide and complete oxidation products $CO_2 + H_2O$, respectively. For the most often encountered consecutive-parallel scheme the selectivity to partial oxidation products decreases with increasing conversion.

Sachtler *et al.* (1971) and Trifiro *et al.* (1971) suggested that the selectivity of product formation in partial oxidation depended on the gradient $dq/d\theta$, where q is the oxygen-catalyst bond energy, and θ stands for coverage. If the yield of complete oxidation products is higher on a surface with a low q value, and that of partial oxidation is higher on a surface with higher θ, then, as oxygen departs from the surface, q will increase and S will change towards partial oxidation products. The greater the surface inhomogeneity, i.e., the gradient $dq/d\theta$, the higher will be the S value. The connection between selectivity and the oxygen mobility in the oxide lattice has already been mentioned.

The relation of catalytic activity and selectivity to the q value of the oxygen-catalyst bond is now being systematically studied (Golodets, 1977). The problem of the relation between selectivity and the active component of the catalyst was also discussed (Pyatnitskii and Golodets, 1976). When both complete and partial hydrocarbon oxidation occur on active sites of the same chemical nature (e.g., on V ions bound with oxygen O^{2-} in V_2O_5 supported on an inert substrate), then the selectivity to partial oxidation products will be stronger with a small number of V atoms in an active site. Conversely, the selectivity to complete oxidation products will be higher with surface clusters, e.g., with a large amount of metal atoms in one cluster. Such a mechanism of the active component concentration effect on selectivity is realized, when the hydrocarbon oxidation follows the mechanism



$$\mathrm{RH} + \begin{array}{cc} \mathrm{O} & \mathrm{O} \\ | & | \\ \mathrm{M}\ldots & \mathrm{M}\end{array} \rightarrow \cdots \begin{array}{cc}\mathrm{RO}_i & \mathrm{OH}\\ | & \backslash \\ \mathrm{M}\ldots & \mathrm{M}\end{array} \rightarrow \begin{array}{ccc}\mathrm{RO}_i & & \mathrm{O}\\ | & + & | \\ \mathrm{M} & & \mathrm{M}\end{array} \rightarrow \begin{array}{c}\mathrm{RO}_{i+1}\\ | \\ \mathrm{M}\ldots\mathrm{M}\end{array}$$

Indeed it was found (Pyatnitskii and Golodets, 1976) for oxidation of *o*-xylene on Al_2O_3-supported V_2O_5 that as the vanadium amount in clusters (surface concentration of V_2O_5) increases, S decreases towards the less oxidized *o*-toluene aldehyde and increases towards the more oxidized phthalic anhydride. The oxygen-catalyst bond energy does not seem to depend on the cluster size.

Similar results have been obtained for oxidative dehydrogenation of butylenes on supported V_2O_5/Al_2O_3 catalysts. It was found that selective butadiene formation occurs at low V_2O_5 concentrations, whereas CO_2 and H_2O are generated at high V_2O_5 concentrations (Nurgalieva *et al.*, 1973). It was suggested from these results (Krylov, 1975) that with an increase in the number of O atoms or O_2 molecules in some activated species (O^-, O_2^-) at the elementary step of C_nH_m reaction the yield of complete oxidation products becomes greater.

The papers cited here in explaining the selectivity of oxide catalysts do not account for one of the basic properties of partial hydrocarbon oxidation catalysts, namely for their phase composition. Yet, as stated at the beginning of this paper, the increase in selectivity of industrial partial oxidation catalysts is connected first of all with the development of polyphase catalysts (*see*, for example, *Fig. 1*).

The role of polyphasicity in redox catalysis has been discussed for a long time. Even Langmuir (1916) noted how difficult it was to interpret such reactions in terms of an equilibrium two-phase system. When one of the stages, e.g., in our case oxidation, occurs on the surface of one phase, its rate will be proportional to the surface of this phase and to the pressure of one of the components (of oxygen)

$$w_1 = k_1 n_1 P_{O2} (1 - \theta_1)$$

where θ_1 is the surface coverage with oxygen, n_1 the number of active sites, k_1 the rate constant. Similarly it can be written for the reaction rate on the other phase surface, for instance for interaction with RH

$$w_2 = k_2 n_2 P_{RH} (1 - \theta_2)$$

If both reactions occur under equilibrium conditions, $w_1 = w_2$, and there is mutual transition of the first and second phases, for instance by oxidation and reduction, this contradicts the phase rule: the phase number (two solid phases and gas) + the number of independent variables (P_{O2}, P_{RH}, T) appears to be higher than the number of components (solid component and two gases, i.e., three + 2). Langmuir (1916) logically inferred from this contradiction that under equilibrium these reactions cannot represent interaction with gases on the surface of each phase and the redox reaction has to occur on the interfacial boundary.

Later (e.g., Wagner and Hauffe, 1938; Bruns, 1947) these Langmuir concepts were extended to a stationary catalytic reaction occurring by the redox mechanism. If k_1 is the rate constant of oxidation per unit metal oxide surface, and k_2 that of reduction, then, according to Wagner and Hauffe (1938), two possibilities arise: either $k_1 P_{O2} > k_2 P_{RH}$ and the reaction will occur on the oxide, or $k_1 P_{O2} < k_2 P_{RH}$ and the reaction will then be on the reduced phase (on metal). Even a fortuitous equilibrium $k_1 P_{O2} = k_2 P_{RH}$ will be disturbed by changes in O_2 and RH concentrations during the reaction. Thus the above authors think that a stationary catalyst must consist of one phase only. In a redox process solid metal ion solutions of different valence and oxygen vacancies will form on the surface.

It will be noted, however, that stationary catalyst activity is not equivalent to equilibrium. Moreover, hydrocarbon oxidation is irreversible and in general has not been studied under equilibrium conditions.

As shown by the first detailed studies (Weisz and Prater, 1954) of polyphase polyfunctional catalysts, the necessity to account for molecular transfer varied for different locations of x and y. Physical transport of intermediates between x and y occurs by diffusion which becomes an important step in the chain of reactions. For a stationary state the diffusion of intermediates can appear to be the limiting step.

For illustration, the above can be compared to a reaction with a temperature gradient in the catalyst. In this case different catalyst regions are under different equilibrium conditions. There is no doubt that during catalysis with gradient $dT/d\theta$ one phase will be stable at one temperature, and the other at another temperature.

There is a boundary between the two phases where the phase transition occurs. Redox catalysis involves not a temperature, but a surface concentration gradient $dc/d\theta$. It comes to the same: to the possibility of the occurrence of catalysis through phase transitions.

It will be noted that surface temperature gradients are also possible for strongly exothermic oxidation reactions (Srivastava *et al.*, 1982). Weisz and Prater (1958) suggested that microphases of several Å with a temperature several scores of degrees different from that of the whole surface might arise during oxidative catalysis. This, in its turn, would result in additional non-equilibrium of the catalyst surface and in diffusion flows.

A peculiar non-stationary reaction regime—the auto-oscillations—has been discovered for a number of catalytic oxidation reactions (Slin'ko and Slin'ko, 1982). These oscillations can be conceived as a transition from one phase to another, e.g., from an oxidized to a reduced phase. The possibility of thermokinetic vibrations with autocatalytic heating of the catalyst by the heat of the exothermal step has also been considered (Slin'ko *et al.*, 1981). After the whole compound in the reactor has reacted, the reaction terminates and then starts again.

The concentration and temperature gradients in such systems make possible a selective reaction development by one of the possible paths. Different reaction steps on a multicomponent polyphase catalyst can be accelerated by the phase surface. Consequently, the first task in obtaining a selective catalyst is a study of the catalytic reaction mechanism, followed by the selection of best catalysts and phases accelerating specific steps. Finally comes the design of a multicomponent catalyst.

Some 50 years ago this method yielded a selective catalyst for butadiene synthesis from alcohol (Lebedev, 1933).

$$C_2H_5OH \rightarrow C_4H_6 + 2H_2O + H_2$$

The creators of this catalyst, S. V. Lebedev and his co-workers, distinguished the stages of the process: dehydration, dehydrogenation, and condensation, and, having found a catalyst for each stage, they designed a multicomponent catalyst consisting of oxide phases accelerating the relevant specific stages.

However, for a multistep reaction, the use of a complicated catalyst might result in greater selectivity than that for consecutive occurrence of the reaction in different reaction zones. Weisz and Prater (1954) found that the trivial polyfunctional catalysis involving reaction

$$A \xrightarrow{x} B \xrightarrow{y} C$$

(the first step $A \rightarrow B$ occurring on phase x, and the second step $B \rightarrow C$ on phase y) must be distinguished from the non-trivial multistep catalysis. For instance, if the yield in the first step is limited by thermodynamic equilibrium

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{k_2} C$$

Here $K_{eq} = k_1/k_{-1}$ the extent of conversion can be very high. The overall reaction rate in this case is

$$\frac{d[A] \quad k_2[A]}{(1/K) + (k_2/k_1)} = k^1 [A]$$

The k^1 value can be made very high by relevant choice of rate constants k_1 and k_2. The A yield will then exceed that obtained from the simple consecutive scheme.

Non-trivial complex catalytic processes also involve catalysis in the separation chromatography regime (Roginskii *et al.*, 1972). In this case the increase in the desired product yield is attained by continuous removal of the product from the catalysis zone accompanied by a shift of equilibrium. The polyphasicity appears to be advantageous in this case as well: one of the phases accelerates catalysis as such, and another ensures the separation of initial and end-products.

Catalysis due to phase transitions on the catalyst surface has been discussed by Berman and Krylov (1976, 1978) and Krylov (1981).

Adsorption and activation of a hydrocarbon on a polyphase catalyst can be conceived to occur on one phase, and of oxygen on another, with subsequent diffusion of oxygen ions along the lattice and of the hydrocarbon complexes towards the interfacial boundary to react there. Selective catalysts must be capable not only of activating the reactants, but also of transporting them to the active sites.

4. PARTIAL OXIDATION SELECTIVITY AND THE CATALYST STRUCTURES

In the papers by Sleight and Linn (1976), the oxide catalysts, with additives, are taken to be monophase systems, the additives creating vacancies in the lattice. Likewise, Trifiro *et al.* (1971) noted that the tellurium-containing catalysts: $CdTeMoO_6$, $CoTeMoO_6$, $MnTeMoO_6$ and $ZnTeMoO_6$ are monophasic, and highly selective in the oxidation of propylene and butylene. A stationary V_4O_9 phase was observed in the oxidation of tetrahydrofuran to γ-butyrolactone on a vanadium oxide catalyst (Scoan, 1980). Finally, it will be noted that the authors of most papers dealing with active sites in molybdate catalysts (*see Table 8*) usually assume that these catalysts are monophasic, but no detailed phase analyses have been conducted to prove this point.

A considerably greater number of papers on partial oxidation catalysts that have been subjected to X-ray phase analysis show that the catalysts are polyphasic. Even when the initial catalyst is monophase, it becomes a polyphasic system after the reaction.

Contrary to the results obtained earlier (Forzatti *et al.*, 1978), Bart and Giordano (1980) showed that in the acrylonitrile catalytic synthesis the Te–MoO catalyst is itself converted to a mixture of phases: TeO_2, $TeMo_5O_{16}$, MoO_2, MoO_{11}. An increase in the number of phases during catalysis has also been observed for the multicomponent Ni–Co–Fe–Bi–Mo–O oxide catalyst in propylene ammonolysis (Prasada Rao and Menon, 1978). The fresh catalyst involves phases $Fe(MoO_4)_3$, β-$CoMoO_4$, $NiMoO_4$, Bi_2O_3 and $Bi_2O_3 \cdot 3MoO_4$. A reduced $FeMoO_4$ phase appears after the reaction. According to ESCA results, the Mo, Bi, Fe content on the surface increases, whereas that of Co and Ni decreases.

Use of the ESCA method in studying molybdenum-containing catalysts, and the fact that redistribution of the components between the surface and bulk takes place, suggested a nut-like, shell-nucleus, structure of the catalyst granule. It has been suggested (Matsuura, 1980) that the Fe–Mo–Bi–O propylene oxidation catalyst involves a Co–Fe–Mo–O phase representing the oxygen source, and electron acceptor. The active MoO_3 + bismuth molybdate phase is distributed over the above phase. Similar views have been reported by Ueda *et al.* (1981). In essence, this is again the principle of catalysis occurring through phase transitions: transport of oxygen occurs at the interfacial boundary.

A unique mechanism, enabling interpretation of the observed regular olefin conversions on complex oxide catalysts has been proposed (Shtyrkov *et al.*, 1972). According to their scheme, oxygen adsorbs on certain active sites Z, and then is transported to other sites K, where it interacts with the olefin

$$O_2 + Z \rightleftharpoons ZO_2^-$$
$$Z + ZO_2^- \rightleftharpoons 2ZO^{2-}$$
$$K + ZO^{2-} \rightleftharpoons KO^{2-} + Z$$
$$ZO_2^- + RH \rightleftharpoons Z + CO_2 + H_2O$$
$$KO^{2-} + RH \rightleftharpoons K + RO + H_2O$$

The high selectivity of multicomponent catalysts ($Bi_2O_3 \cdot Fe_2O_3 \cdot MoO_3$ or $Bi_2O_3 \cdot Fe_2O_3 \cdot NiO \cdot Co_2O_3 \cdot Fe_2O_5 \cdot MoO_3$) seems to be due to possible involvement of several cations in O^{2-} transport and to spatial separation of the Z and K states. Oyxgen differing from the lattice oxygen reacts at the Z sites, and this can result in extensive oxidation.

The Fe–Mo–O catalyst for selective oxidation of methanol to formaldehyde must involve, alongside the $Fe(MoO_4)_3$ phase, an excess of the MoO_3 phase. Stabilization of phases on the α-Al_2O_3 support surface favours the stable activity of the catalyst (Cotter *et al.*, 1982).

Still more papers have been published on the polyphasicity of vanadium pentoxide-based selective oxidation catalysts. Arguing against Scoan (1980), for the stationary oxygen-induced oxidation of tetrafuran to γ-butyrolactone, Srivastava *et al.* (1982) stated that, according to *in situ* X-ray measurements, the vanadium oxide catalyst contains two phases: V_4O_9 and V_2O_5. It was suggested that V_2O_5 is present in a stationary state, as an admixture with V_2O_4.

Vejux and Courtine (1978) showed that addition of anatase (TiO_2) to vanadium pentoxide resulted in a process they called 'topotactic reduction', which lowered the activation barrier for reduction. This process is related to the specific vanadium–titanium catalyst structure. ***Figure 5*** presents a part of such a structure favouring the conversion of the catalyst components. Anatase converts to rutile at much lower temperatures than those in the absence of vanadium ions, and the tetravalent vanadium ions become stabilized in rutile, which is needed for oxidation of aromatics. It has been shown in the recent paper by Kozlowski *et al.* (1983) by the EXAFS technique that the TiO_2 supported V_2O_5 catalytically active surface phase is not in epitactic registry with the TiO_2, but is in a state of structural disorder.

A similar V_2O_5–TiO_2 system has been studied (Anderson and Lundin, 1980) as catalyst for oxidative ammonolysis of γ-picoline to nicotine nitrile. A solid solution of V^{4+} in TiO_2 was found (Yabrov *et al.*, 1975) in similar *o*-xylene oxidation catalysts. However, catalysts with a high content of this solid solution (90%) were less active. On the basis of the X-ray phase analysis it was suggested (Cole *et al.*, 1976) that the atoms at the V_2O_5–V_6O_{13} boundary represent the active sites, formation of V_6O_{13} being readier in the presence of TiO_2.

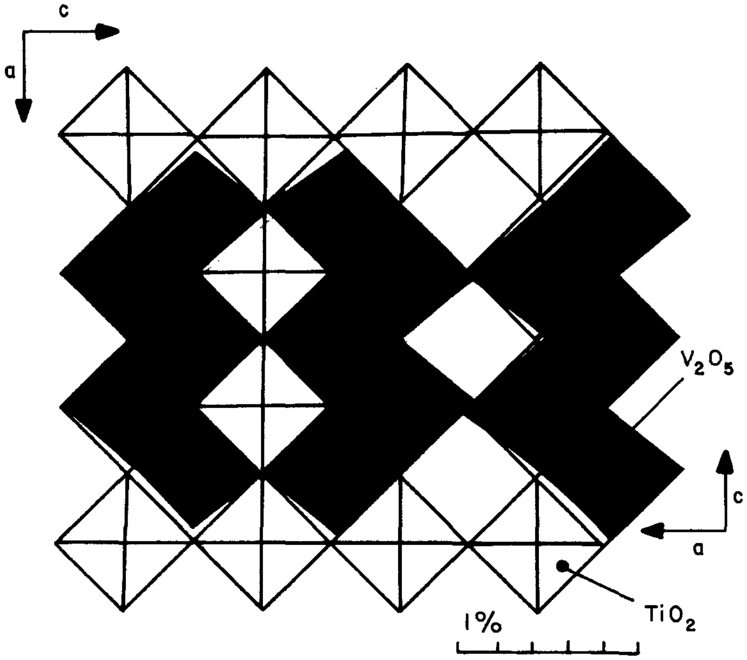


FIG. 5. Schematic fragment of a vanadium-titanium catalyst structure (Vejux and Courtine, 1978).

Microdomains $VOPO_4$ and larger formations $(VO_2)P_2O_7$ have been found in the vanadium phosphorus catalyst for butylene oxidation to maleic anhydride. It has been suggested by Bordes and Courtine (1979) that the active sites are located at the boundary between these phases. The boundaries are coherent: they represent planes (203)$VOPO_4$ and (102)$(VO)_2P_2O_7$. The same ratio was observed for V_2O_4 and V_6O_{13}. Bordes and Courtine (1979) think that the lattice relaxation during catalysis is slower compared to a strictly redox process. A strained lattice forms during reduction, and excess energy is imparted directly to the catalytic reaction.

A segregation of both elements was observed (Bielanski *et al.*, 1979) in the $V_2O_5 \cdot MoO_3$ system after reduction. The vanadium ions diffuse into the lattice in the course of reduction. An intermediate compound $V_9Mo_6O_{40}$ and a phase V_2O_5 enriched with Mo are formed.

A two-phase system has also been observed in stationary benzene and xylene oxidation on $V_2O_5 \cdot MoO_3$ (Ioffe *et al.*, 1962). It was suggested that a thermodynamic non-equilibrium state of the catalyst arises under these conditions.

A maximal activity of the MoO_3, TiO_2 catalyst in the selective oxidation of 1-butylene and butadiene has been attained with a two-phase catalyst, the active sites being located at the interfacial boundary (Vanhove *et al.*, 1979).

Segregation of antimony as a Sb_2O_4 phase was observed in the $Sn_{1-x}Sb_xO_2$ catalyst (Cross and Pyke, 1979).

The many papers concerned with catalysis on solid oxide solutions of transition metal elements M (e.g., Co, Ni, Mn) in oxides of non-transition elements M^2: $M^1_x M^2_{1-x}O$ (*see* review by Krylov and Kiselev, 1981) will also be mentioned. Kadushin (1983) found from measurements of the magnetic susceptibility that during oxidation catalysis at 300–400°C the atoms (ions) of the Co or Ni transition metal are not statistically distributed in the MgO matrix, but form clusters. The Co^{2+} or Ni^{2+} ions can interact in the clusters by indirect exchange M^1–O–M^1. The catalytic activity of atoms in clusters differs from that of isolated atoms. Thermodynamic calculation shows that equidistribution of the M^1 and M^2 ions between the surface and bulk is attained only at temperatures of about 1000°C. At low temperatures the transition element segregates on the surface (Highfield *et al.*, 1982). The reduction and reoxidation of solid $Co_xMg_{1-x}O$ and $Ni_xMg_{1-x}O$ solutions at 300–400°C were found to yield microparticles NiO and CoO (or Co_3O_4) that passed to the solid phase at 600°C only (Shiryaev *et al.*, 1983).

Thus, without denying the role of solid solutions in oxidation catalysis, it can still be claimed that, even in binary oxide systems, two and more phases are often formed during catalysis. Cullis and Hucknall (1982) stated more definitely that solid solutions are of minor importance in catalysis. The multicomponent catalysts are virtually always polyphasic.

The structure of the widely used Bi–Fe–Co–Mo–O catalyst has been studied in detail by Margolis (1977) and co-workers using various physical methods. Prior to the onset of catalysis, it consists of four basic phases: cobalt *β*-molybdate, bismuth

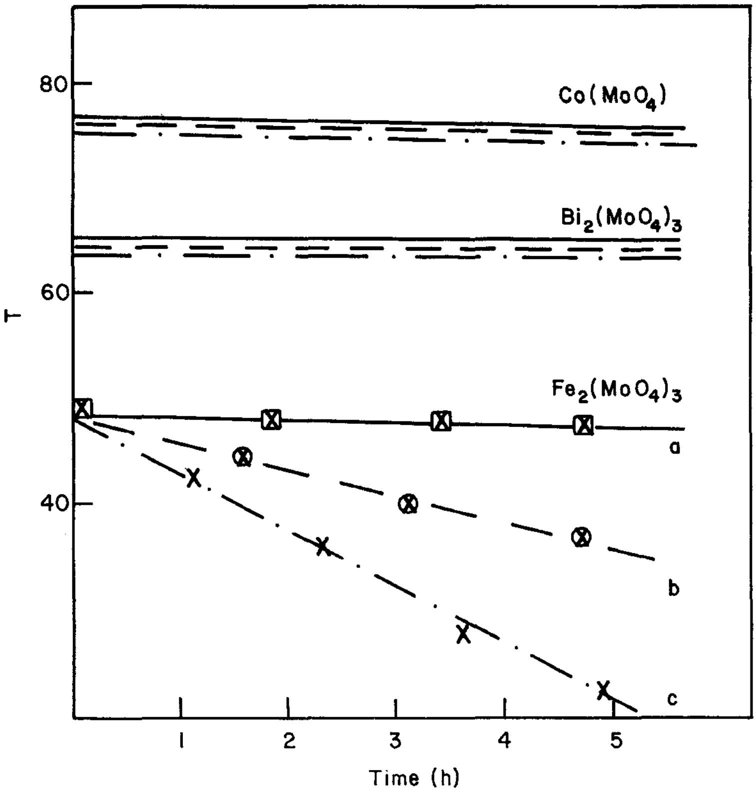


FIG. 6. Changes in intensity of the X-ray line characteristic of the structures of individual molybdates as a function of the Co–Mo–Bi–Fe–Sb–K catalyst composition. a = C_3H_6:O_2;1:3; v = 1:2; c = 1:1.

α-molybdate, iron molybdate, and excess molybdenum oxide. Iron molybdate stabilizes on the surface of other molybdates. The crystal lattices of $Fe_2(MoO_4)_3$ are coherent with the $Bi_2(MoO_4)_3$ lattice and can even form mixed $Bi_2Fe(MoO_4)_3$ crystals, as are detectable by Mössbauer spectroscopy.

The conversions of this catalyst in the course of catalysis were studied by measuring the X-ray structure and Mössbauer spectra *in situ*, i.e., during catalysis (Shashkin and Maksimov, 1983; Shiryaev *et al.*, 1983). The phase transitions in a Co–Mo–Fe–Sb–Bi–K catalyst were studied for propylene oxidation in a reactor connected with the X-ray camera (*Fig. 6*) (the mixture content was varied: 1:3, 1:2, 1:1). It appeared that the phases of cobalt and bismuth molybdates on the whole remained unchanged in the course of catalysis, whereas the iron molybdate was most labile and with an increased olefin concentration in the gas it converted to β-$FeMoO_4$.

Despite the decrease in tervalent iron concentration in the system, the activity and selectivity of propylene oxidation remain the same. Probably the surface contains ions, both Fe^{3+} and Fe^{2+} or relevant nuclei ensuring electron transfers and migration of oxygen during re-oxidation, and thus the changes in tervalent iron content in the bulk seem to be connected with catalysis in a more complicated way. Under the same conditions pure iron molybdate suffers no change and this indicates the effect of polyphasicity of the highly selective catalyst on the reduction of the labile tervalent iron molybdate. The Mössbauer spectrum of iron ions in Co–Mo–Bi–Fe–Sb–K (*Fig. 7*) before reaction is that of $Fe_2(MoO_4)_3$ and after reaction that of β-$FeMoO_4$. The X-ray, Mössbauer spectroscopy, microcalorimetry techniques, impact compressions, and shear deformation at high pressures, as well as the experiments in the course of catalysis, revealed the following reactions of crystalline iron molybdate conversions:

$$Fe_2(MoO_4)_3 + 3Bi_2(MoO_4)_3 \rightarrow 2Bi_3FeMo_2O_{12} + 8MoO_3$$

$$Fe_2(MoO_4)_3 \xrightarrow{+C_3H_6} 2FeMoO_4 + MoO_3$$

$$Fe_2(MoO_4)_3 \xrightarrow{C_3H_6+O_2} 2FeMoO_4 + MoO_3$$

$$Fe_2(MoO_4)_3 \xrightarrow{\text{impact compression}} \begin{matrix}\text{amorphous}\\ \text{molybdate}\end{matrix} \rightarrow 2FeMoO_4 + MoO_3 + 1/2O_2$$

As shown by specific experiments the replacement of β-$CoMoO_4$ by $MgMoO_4$ of the same crystallographic structure in the complex Bi–Fe–Co–Mo–O catalyst has no effect on the redox activity of the catalyst. It seems that Co, as well as Mg, ions are not involved in the redox process. The latter is ensured by Fe^{2+}–Fe^{3+} ions and the MoO_3 and $Bi_2(MoO_4)$ phases, and occurs at the interfacial boundary. The summary equations for lattice reduction and oxidation (Krylov and Kiselev, 1981) can be written as

$$C_3H_6 + 2Fe^{3+} + MoO_3 + O^{2-} \rightarrow C_3H_4O + 2Fe^{2+} + MoO_2 + H_2O$$

$$O_2 + 2Fe^{2+} + M^{2+}MoO_3 \rightarrow O^{2-} + 2Fe^{3+} + M^{2+}MoO_4$$

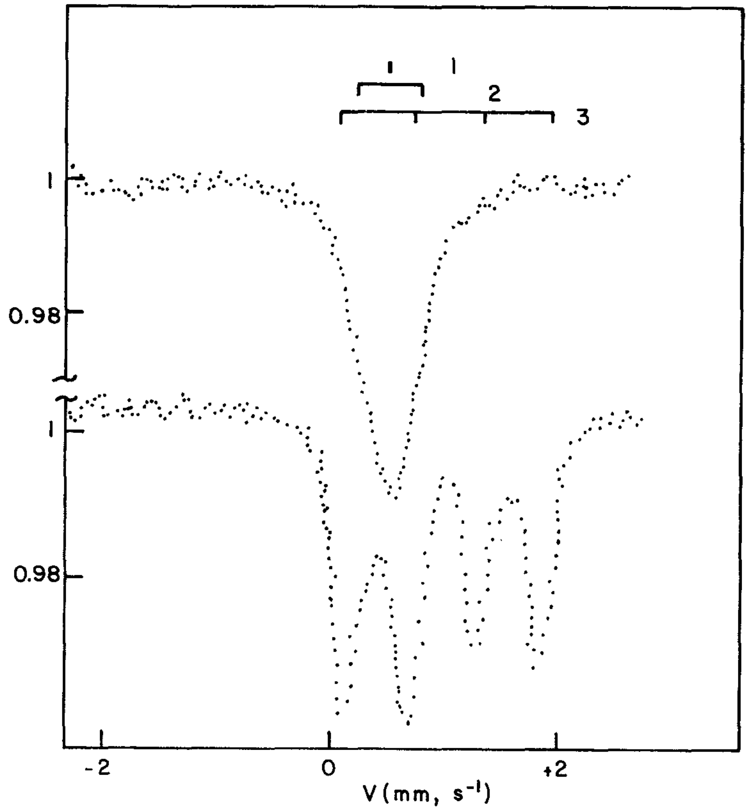


FIG. 7. Mössbauer spectra of iron ions in Co–Mo–Bi–Fe–Sb–K catalyst before and after reaction (C_3H_6:O_2 = 1:1).

with subsequent electron and oxygen exchange at the interfacial boundary

$$2Fe^{2+} + MoO_2 + 2Fe^{3+} + M^{2+}MoO_4 \rightarrow (2Fe^{3+} + MoO_3) + (2Fe^{2+} + M^{2+}MoO_3)$$

Haber *et al.* (1983) have reported that the reconstruction of oxide structures favours the removal of oxygen from the catalyst.

Oxidation of olefins to unsaturated aldehydes, oxidative ammonolysis and oxidative dehydrogenation of olefins occur on similar catalysts. As stated above, the mechanisms of these reactions are related to strongly bound lattice oxygen interacting with the weakly bound hydrocarbon (possibly with an allyl complex). This interaction seems to occur at the interfacial boundary.

Other reactions of partial oxidation can follow different mechanisms. For instance, the formation of saturated aldehydes and ketones from olefins depends on the Bronsted acidity of the surface and this is greater in the presence of water.

Another mechanism of selective oxidation involving heteropoly acids has been discovered recently (Ai, 1981). The oxidation of methacrolein to methacrylic acid at 200–300°C is accelerated by 12-molybdenum-phosphorus heteropoly acid $H_3PMo_{12}O_{40}$ and its salts $Ca_{3/2}PMo_{12}O_{40}$, $Na_2HPMo_{12}O_{40}$, etc. Tungsten-based

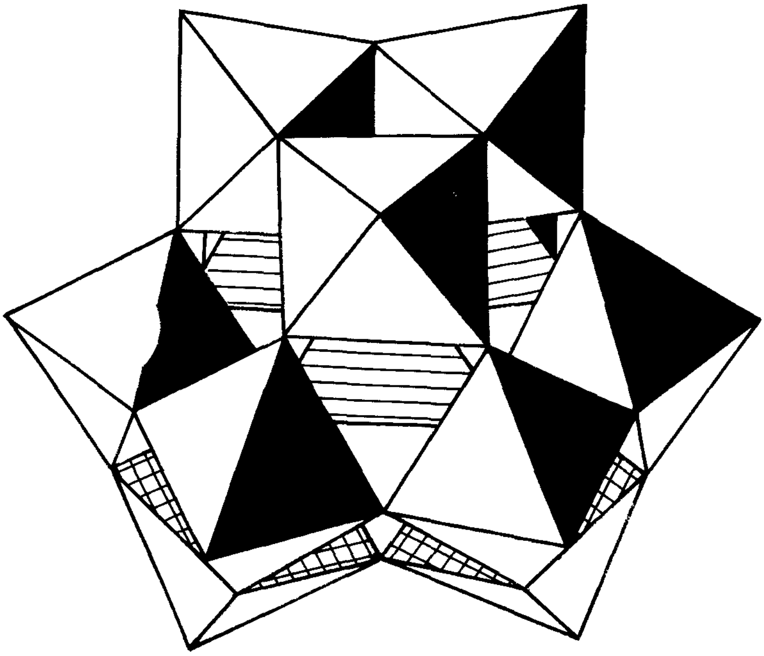


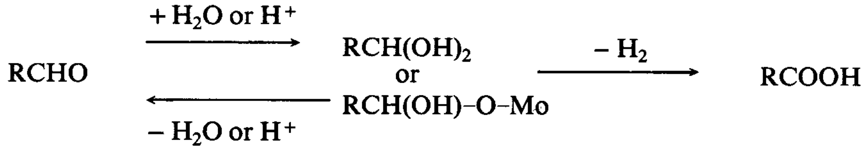
FIG. 8. Polyhedral representation of the Keggin structures of heteropoly acids.

heteropoly acids—$H_3PW_{12}O_{40}$, $H_3PW_6Mo_6O_{40}$ and $H_3SiW_{12}O_{40}$—were also studied. All these compounds are of a Keggin structure consisting of twelve MoO_6 or WO_6 octahedra surrounding a PO_4 or SiO_4 tetrahedron (*Fig. 8*). The crystal lattice of heteropoly acids contains also cations (Ca, Na, etc.) and water of crystallization.

The activity of such catalysts is proportional not to the surface area, but to the bulk of the supported heteropoly acid. This points to the possibility of the occurrence of reaction in microcavities of the crystal lattice, as with reactions in zeolites. The selectivity might be connected here with the matrix effect. The most active and selective systems were found to be: $H_3PMo_{12}O_{40}$, $CuPMo_{12}O_{40}$, $CsPMo_{12}O_{40}$-$H_3SiMo_{12}O_{40}$, $H_3V_2Mo_{10}O_{40}$. The tungsten systems were less active and selective. Removal of water from the system resulted in a marked decrease of activity and selectivity, which suggested a relation between catalytic activity of heteropoly acids and their proton acidity. This suggestion was confirmed by experiments using pyridine. Pyridine absorbed by the heteropoly acid formed a $C_5H_5NH^+$ ion, and the catalytic activity decreased linearly with growing amounts of absorbed pyridine.

Partial oxidation on heteropoly acids has been studied further (Ai, 1981; Akimoto *et al.*, 1981; Goncharova *et al.*, 1982; Kenishi *et al.*, 1982; Shokhireva *et al.*, 1982).

It appeared (Ai, 1981) that at 200–400°C ethylene, propylene and benzene almost do not oxidize on $H_3PMo_{12}O_{40}$; 1- and 2-butylenes oxidize to maleic anhydride and carbon dioxide with butadiene to furan and CO_2, furan to maleic anhydride, acrolein to acrylic acid, methylethylketone to acetic acid and acetaldehyde, methanol to formaldehyde. Supported heteropoly acids also appeared to be active in purely acidic alcohol dehydration and olefin isomerization. Thus, an acidic oxidation mechanism of aldehydes to acids was proposed:



$$\mathrm{RCHO}\ \underset{-\,H_2O \text{ or } H^+}{\overset{+\,H_2O \text{ or } H^+}{\rightleftarrows}}\ \begin{matrix}\mathrm{RCH(OH)_2}\\ \text{or}\\ \mathrm{RCH(OH)\text{-}O\text{-}Mo}\end{matrix}\ \xrightarrow{-\,H_2}\ \mathrm{RCOOH}$$

The oxidation activity of $H_3PMo_{12}O_{40}$ was suggested (Ai, 1981) to be too weak for the C_2 and C_3 olefin oxidation and to be sufficient only for unsaturated aldehydes, methylethylketone and C_4 olefins.

The Keggin structure was reported (Kenishi *et al.*, 1982) to suffer no disturbance during catalytic oxidation and reduction

$$H_3PMo_{12}^{VI}O_{40} \xrightarrow{+H_2} H_3PMo_2^{V}Mo_{10}^{VI}O_{40} \rightarrow H_3PMo_2^{V}M_{10}^{VI}O_{40} + H_2O$$

The heteropoly acids were reported (Goncharova *et al.*, 1982; Shokhireva *et al.*, 1982) to form also on MoO_3 supported on compounds often used in selective oxidation. For instance, the interaction of TiO_2 with ammonium paramolybdate yields the Ti–Mo heteropoly acid fixed on titanium dioxide and detected in IR absorption spectra.

CONCLUSION

The origin of catalyst selectivity in the partial oxidation of hydrocarbons and other organic compounds cannot be considered as elucidated. Yet the recent studies on the stepwise mechanisms of such reactions enable certain conclusions to be drawn.

1. Partial oxidation occurs by a redox mechanism involving oxygen of the oxide catalyst lattice.
2. Partial oxidation involves strongly bound oxygen in the form of O^{2-} ions, or oxygen doubly bound with molybdenum, vanadium, and ions of related elements.
3. Olefin molecules interact with the catalyst surface to form relatively weakly bound or allylic dehydrogenated complex.
4. The above complex diffuses towards the active site, where it reacts with the strongly bound oxygen (or with another hydrocarbon–oxygen complex containing strongly bound oxygen).
5. The oxygen can diffuse to the active site through the bulk of the appropriate oxide catalyst.
6. In multicomponent partial oxidation catalysts the active sites are located at the interfacial boundary (or close to it). Rearrangement of the structure in the course of the process can facilitate the formation of the boundary.
7. The greatest selectivity in partial oxidation catalysts is attained with polyphasic multicomponent catalysts, where different phases accelerate different steps of the overall catalytic oxidation process with possible diffusion of intermediates from one phase (one group of active sites) to another.
8. The activation of hydrocarbons of different structure (except for some specific olefins) is related to the acid–base active sites on the surface.

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