SELECTIVITY IN HETEROGENEOUS CATALYTIC OXIDATION

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Abstract — Selectivity of the catalytic oxidation of hydro-
carbons is discussed in terms of the type of intermediate
complex formed. Two different intermediate complexes initiate
two different routes of the reaction. Activation of oxygen
leads to total oxidation through electrophilic attack on the
double bond and formation of the complex of the peroxide or
epoxide type, whereas partial oxidation requires activation
of the hydrocarbon molecule resulting in the formation of
the allyl species bonded as ligand in the intermediate
complex. It proceeds then in a series of consecutive oxidative
elementary steps, each of them requiring different active
centers to be present at the catalyst surface. The type of
product obtained and its selectivity depend thus on the
type and mutual proportions of these centers. Oxidation is
performed by the cationic active centers, whereas oxygen is
inserted by a nucleophilic attack which may also be conside-
red as an acid-base process. Mechanisms of these elementary
steps is are discussed on the basis of the quantum chemical
description of intermediate complexes.

Reactions of the catalytic oxidation of hydrocarbons have been
studied extensively in the past decade/1-4/ because of their great importance
for the development of chemical industry. The introduction of bismuth
molybdate as catalyst for the selective oxidation of propylene to acrolein
by Veatch and Callahan /5/ and the development of the synthesis of acrylo-
nitrile by ammoxidation of propylene on this catalyst may be considered as
turning points in the history of modern petrochemistry /6/. However, also
some of the older catalytic processes such as oxidation of naphthalene and
o-xylene to phthalic anhydride found considerable interest because of the
fact that although they have been operated in industry for many decades, their
mechanism is not yet understood. On the other hand catalytic oxidation of
hydrocarbons is very interesting from the theoretical point of view, as the
organic molecule can in most cases react at the surface along several
different reaction paths, giving several different products. Often small
modification of catalyst composition or variation in the method of its
preparation can modify its catalytic properties to such an extent, that the
direction of the reaction is changed and a new product is formed, usually
with high selectivity. This creates particularly favourable conditions for

studying the correlation between properties of the catalyst and the
selectivity of its catalytic performance, which enables important conclu-
sions to be drawn, concerning the theoretical basis for the selection of
catalysts.

        Selectivity of catalytic reactions may be discussed in terms of the
type of intermediate complex formed at the surface of the catalyst in the
course of the reaction. Three limiting cases may be distinguished as shown
in Fig.1:

a/ from a given substrate the same intermediate complex is always formed,
   but depending on the catalyst the potential barrier along different
   reaction coordinates is lowered and different products are thus formed;
b/ depending on the catalyst different intermediate complexes are formed,
   which then transform into different products;
c/ in a series of consecutive steps several intermediate complexes are
   formed which either desorb to give one of the intermediate products, or
   transform consecutively into each other.

        Ample experimental evidence indicates that highly reactive adsorbed
oxygen radicals are responsible for the reactions of the total oxidation of
hydrocarbons. Results of the study of oxygen isotope exchange and of
tracer experiments with oxygen isotopes are particularly relevant.
Comparison of numerous data on the rate of homomolecular exchange of oxygen
on various transition metal oxides, determined by Boreskov and his school
/7,8/ with the data on catalytic activity of these oxides in the total
oxidation of several simple compounds revealed a close correlation between
the ability of the oxide to activate oxygen and its activity in the
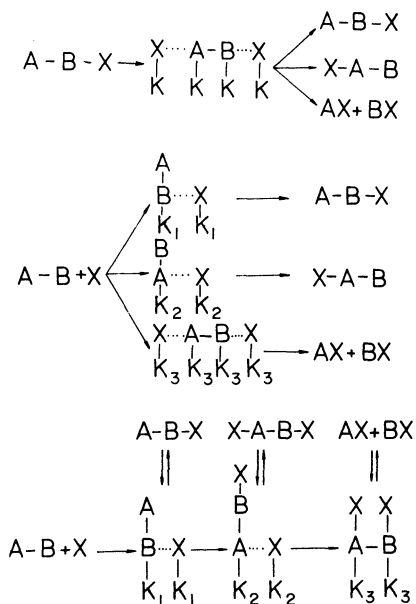catalytic reaction.

Fig.1. Role of intermediate complex in determining the
selectivity of the catalytic reaction.

On the other hand Keulks et al /9/ have shown that when propylene
is oxidized in oxygen containing ^{18}O, this isotope does not at the
at the beginning of the reaction appear in acrolein. This indicates that lattice
oxygen and not the adsorbed one is involved in selective oxidation.
Classical experiments described by Sachtler /1,10/, in which oxidation over
oxide catalysts was carried out with propylene labelled by 14_C in the
α-carbon position, have shown that in the resulting acrolein 14_C is evenly
distributed between both terminal carbons. This was taken as a proof that
in the first step of the reaction propylene is activated by abstraction of
α-hydrogen and formation of an allylic species.

Thus the general conclusion may be formulated that two different
intermediate complexes /case b/ initiate two different paths of the reaction
of catalytic oxidation of hydrocarbons, one leading to partial oxidation
products and the second resulting in total oxidation. Partial oxidation
requires activation of the olefin molecule, resulting in the formation of
the allyl species bonded as a ligand in the intermediate complex, but no
activation of oxygen should take place. The catalyst to be selective in
allylic oxidation should not contain at the surface any adsorbed oxygen.
Heterogeneous activation of oxygen leads to total oxidation. Oxygen,
adsorbed in form of O_2^- or O^- species is a strongly electrophilic
reagent which attacks the organic molecule in the region of its highest
electron density, i.e. at the double bond in the case of olefin, forming an
intermediate complex of the peroxide or epoxide type.

Many observations indicate /11,12/ that adsorbed oxygen species
transform at the surface of an oxide according to the general scheme:

$$O_2/ads/ \longrightarrow O_2^-/ads/ \longrightarrow O^-/ads/ \longrightarrow O^{2-}/lattice/$$
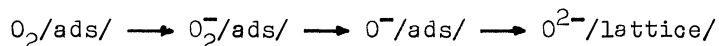
in which they are gradually enriched with electrons.
Depending on the properties of the solid and the experimental conditions
certain transformations may be faster or slower and usually only one
form is predominant in the steady-state. From this point of view all the
oxide catalysts may be divided into three groups /13/. The first group
comprises oxides characterized by high concentration of centers which can
supply electrons to the adsorbed oxygen molecules. These are oxides showing
p-type semiconductivity, as this property is related to the presence of
transition metal cation of low ionisation potential. At their surface oxygen
is adsorbed predominantly in the form of electron rich species. Second group
of oxides is characterized by a low concentration of electron donor centers.
These are n-type semiconducting oxides, diluted solid solutions of transi-
tion metal ions in diamagnetic matrices or transition metal oxides highly
dispersed on cariers. They adsorb oxygen in the form of species less rich
in electrons. Third group is formed by mixed oxides of the oxysalt type
in which oxygen atoms are present in form of well defined oxyanions
with the transition metal ion at its highest oxidation state as the central
atom. Studies of the adsorption of oxygen on different series of transition
metal oxysalts showed /14,15/ that it rapidly decreases with increasing
ionisation potential of the transition metal cation and increasing covalency
of bonds in the anionic group. This may be interpreted in terms of
decreasing electron donor properties of transition metal ions at the surface

$CH_2=CH-CH_3$

First hydrogen abstraction on
transition metal cation

$CH_2-CH-CH_2$ + $CH_2-CH-CH_2$ $\xrightarrow{\text{dimerization}}$ $CH_2=CH-CH_2-CH_2-CH=CH_2$

O^{2-} Me^{+n} O^{2-} O^{2-} Me^{+n} O^{2-}

First oxygen insertion on Mo O
polyhedra and second hydrogen
abstraction

$CH_2-CH-CH_2$ ⎯⎯⎯⎯⎯⎯⎯⎯ $CH_2=CH-\overset{H}{\underset{}{C}}O$

O^{2-} Mo^{+6} O^{2-} O^{2-} Mo^{+4} $\square$

Second oxygen insertion on
acid-base centers

$CH_2=CH-C-O$ ⎯⎯⎯⎯⎯⎯⎯ $CH=CH-COOH$

O^{2-} Mo^{+6} O^{2-} O^{2-} Mo^{+4} $\square$
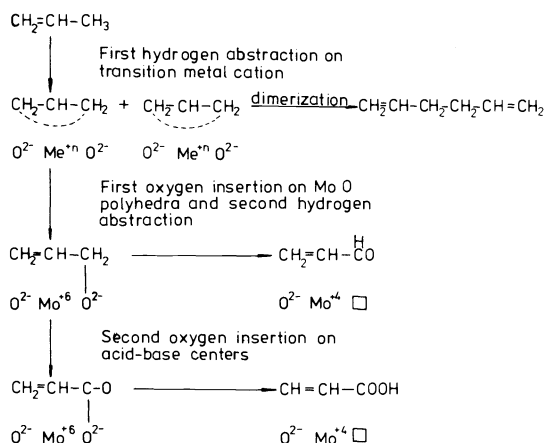
Fig.2. Mechanism of the selective oxidation of olefins.

of the solid with decreasing ligand fields of oxygen ions due to the change
of polarisation of bonds within anionic group.

Reaction path leading to partial oxidation, may be considered as a
series of consecutive oxidative steps, each of them consisting in one ele-
mentary transformation of the reacting molecule and formation of a different
intermediate complex /case c/. Some years ago we have advanced a multicenter
model of such processes /16,17/. Main features of this model are /Fig.2/:
- activation of the olefin molecule, consisting in the abstraction of
  α-hydrogen and formation of π-bonded allylic species, takes place on
  cationic active centers. In the case of molybdates, tungstates etc. these
  centers involve oxygen polyhedra of such cations as Bi^{+3}, Co^{+2}, Ni^{+2} etc.;
- when no other centers are present at the surface, the π-allyl species
  recombine to give dimers of diene type or form polyenes by repetition of
  the first step on cationic active centers;
- different active centers at catalyst surface are required for the inser-
  tion of oxygen. Oxygen polyhedra of molybdenum, tungsten etc. are involved
  in creation of these centers, on which the allylic species transform into
  allyl species σ-bonded to lattice oxygen ions of these. They may
  desorb in the form of aldehyde leaving an oxygen vacancy on the surface
  of the catalyst,
- third type of active centers is involved in the insertion of a second
  oxygen atom into the organic molecule, resulting in the formation of a
  carboxylate intermediate complex, which then desorbs in the form of acid.

In order to study in more detail the role of the metal cations in
the first step of the reaction a series of isostructural compounds:
a-$CoMoO_4$, $NiMoO_4$, $MnMoO_4$ and $MgMoO_4$ was investigated in the oxidation of
propylene to acrolein /18/. Results of the pulse reactor measurements are
summarized in Table 1. As seen from this table, a-$CoMoO_4$ and $MnMoO_4$ show
considerable selectivity in the formation of acrolein, whereas $MgMoO_4$ is
completely inactive. The sublattice of Mo-O polyhedra being identical, this

TABLE 1. The activity of the isostructural molybdates $CoMoO_4$, $MnMoO_4$ and $MgMoO_4$ and the related oxides in their interaction with propylene[x] /18/

Catalyst	Temp. (°C)	Conversion of C_3H_6 /%/	Selectivity /%/ C_3H_6O	C_6H_6	CO_2	Other products
$-CoMoO_4$	490	95	30	10	50	cracking
$MnMoO_4$	490	30	36	-	39	cracking
$MgMoO_4$	490	10	-	-	100	
CoO	450	95	-	30	20	cracking
MgO	490	4	-	-	100	

[x]Pulse method: 1 pulse = 10.2×10^{-6} mol C_3H_6

difference must be due to differences in the properties of cationic active centers. To find which properties of the cation are relevant to the ability to activate the olefin molecule, quantum chemical calculations have been carried out /19/ of the charge distribution, electronic configuration and orbital energy of hypothetical first intermediate surface complexes of metal cations assumed to be octahedrally coordinated by five identical oxygen ligands, the sixth ligand being the allyl radical. Some of the results of the calculations by the SCCC MO method are shown in Table 2. In the case of Co^{+2} and Ni^{+2} complexes there is a considerable shift of π-allyl electrons to the metal, the positive charge appearing thus on the allyl ligand, whereas in Mg^{+2} complexes the allyl remains neutral indicating a very weak binding. Comparison of these data with the catalytic activity of Co, Ni and Mg molybdates /cf. Table 1/ leads to the conclusion that ability of the cation

TABLE 2. Results of theoretical calculations /19/

Metal	Number of unpaired electrons in the complex ion	Average number of π-electrons on allyl	Populations in allyl orbitals π_1^b	π_2^n	π_3^a	Charge on carbon atoms /in e units/ Terminal π-Electronic contribution	Total charge	Central π-Electronic contribution	Total charge
-	1	3	2	1	0	-0.025	-0.096	0.050	0.057
Co^{2+}	4	2.426	1.301	1.039	0.086	0.119	0.048	0.347	0.354
Co^{2+}	0	1.478	1.429	0.027	0.021	0.606	0.535	0.310	0.317
Ni^{2+}	3	2.318	1.284	1.021	0.013	0.149	0.078	0.383	0.390
Ni^{2+}	1	1.365	1.286	0.068	0.011	0.625	0.554	0.383	0.390
Mg^{2+}	1	2.849	1.800	1.033	0.016	0.007	-0.064	0.136	0.143
Mo^{6+}	1	0.836	0.768	0.053	0.015	0.768	0.697	0.627	0.634
Mo^{5+}	2	1.039	0.901	0.123	0.015	0.699	0.628	0.564	0.571
Mo^{5+}	0	0.905	0.828	0.053	0.023	0.750	0.769	0.594	0.601
Mo^{4+}	3	1.046	0.903	0.123	0.020	0.687	0.616	0.561	0.568
Mo^{4+}	1	1.203	0.962	0.228	0.013	0.633	0.562	0.536	0.544

to bind π-allyl is a condition necessary for its role as the active center of the first step of the reaction.

As in the majority of the partial oxidation reactions the first step is rate determining, studies of these reactions cannot yield any information on the next stages of the reaction. One of the ways by which the discussed model could be confirmed and the mechanism of the insertion of oxygen studied in more detail, is to by-pass the first step by generating the allyl radicals by some other more effective route. This was effected [20] by using allyl iodide, which readily decomposes into allyl radicals. The first step of the selective oxidation is thus facilitated, making possible the examination of the conditions which are necessary for the insertion of oxygen in the next step of the reaction.

Important conclusions may be drawn from the comparison of the behaviour of Bi_2O_3 and MoO_3 in the reactions with propylene and allyl iodide /Table 3/. When allyl iodide is passed over MoO_3, already at $310^{\circ}C$ practically total conversion is observed with 98 % selectivity to acrolein. In the same conditions MoO_3 is completely inactive with respect to propylene. On contacting allyl iodide with Bi_2O_3, total conversion at 310° was also observed. In this case however 70 % of the products formed was 1,5-hexadiene, practically no acrolein being detected. Comparison with the results for homogeneous reaction indicates that hexadiene was formed mainly as the result of heterogeneous reaction at the surface of Bi_2O_3, because at 310° only about 20 % conversion is observed in homogeneous reaction. 1,5-Hexadiene as the product was also obtained in the reaction of propylene on Bi_2O_3. These results confirm the validity of the multicenter model of molybdate catalysts, which we have advanced. As the role of Bi-centers in selective oxidation catalysts consists in generation of allyl species, change of the reactant from propylene to allyl radicals formed in situ in the reactor as the result of the decomposition of allyl iodide does not change the reaction pattern, only higher yield of 1,5-hexadiene is observed. Different situation exists in the case of MoO_3. Its surface contains active centers which are able to
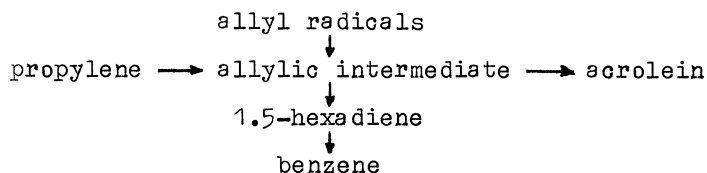
TABLE 3. Interaction of propylene and allyl iodide with
molybdates /20/

Catalyst	PROPYLENE				ALLYL IODIDE				
	Temp. $^{\circ}C$	Yield, %			Temp. $^{\circ}C$	Yield, %			
		Hexa-diene	Ben-zene	Acro-lein		Propy-lene	Hexa-diene	Ben-zene	Acro-lein
Bi_2O_3	480	8.6	–	–	310	– (2.0)	70.0 (8.0)	– (–)	5.0 (–)
MoO_3	480	–	–	–	310	–	–	–	98.0 (–)
Bi_2MoO_6	460	–	–	13.0	310		12.0	3.0	15.0
$Mg_2Mo_3O_{11}$	480	–	–	1.0	370	15.0 (25.0)	10.0 (25.0)	– (2.0)	25.0 (–)
$MgMoO_4$	480					61.0 (62.0)	0.7 (7.0)	1.3 (7.0)	– (–)

Numbers in brackets – homogeneous reaction

perform the insertion of oxygen into the organic molecule. However MoO_3 is inactive in propylene oxidation because no centers are available for efficient generation of allylic species. When, however, such species are formed by some other route, their total convertion to acrolein at MoO_3 surface takes place.

An efficient catalyst for the oxidation of propylene to acrolein is therefore characterised by two functions: activation of propylene by formation and bonding of allylic species, and insertion of oxygen into the hydrocarbon molecule. In complex oxide catalysts these functions are played by different lattice constituents as Bi-O and Mo-O polyhedra, However, it may also be visualised that a single oxide has both kinds of centers present at the surface. The overall reaction may be described by a series of of consecutive, parallel steps:

$$\begin{array}{c}
\text{allyl radicals} \\
\uparrow \\
\text{propylene} \longrightarrow \text{allylic intermediate} \longrightarrow \text{acrolein} \\
\downarrow \\
\text{1.5-hexadiene} \\
\downarrow \\
\text{benzene}
\end{array}$$

Even when both kinds of active centers are present at the surface of the catalyst as it is the case in Bi_2MoO_6, the acrolein/diene ratio will depend on the ratio of the rate constants. In the case of the oxidation of propylene, its adsorption (which is equivalent to its activation to allylic intermediate) is rate determining [21]. In such conditions the surface of the catalyst is scarcely populated with allylic intermediates, which immediately react to acrolein, the selectivity of this product thus being very high. When however the surface is contacted with allyl radicals generated in the gas phase by decomposition of allyl iodide, the coverage of the surface with adsorbed allylic intermediate may attain much higher values and the probability increases that two such species will be adsorbed at adjacent centers and recombine to form 1,5-hexadiene. Table 3 shows that in fact the reaction of the allyl iodide at the surface of Bi_2MoO_6 results in the formation of certain amount of 1,5-hexadiene and benzene and consequently much lower selectivity to acrolein than that observed in oxidation of propylene. When active centers for oxygen insertion are removed by replacing molybdate anions with e.g. phosphate, the reaction path to acrolein is eliminated and high conversion to benzene is observed [22].

Some time ago Seiyama et al [23], Golodets [24] and Ai [25] advanced a hypothesis that different behaviour of oxides in the oxidation of hydrocarbons may be related to their acid-base properties. Although this parameter is certainly of great importance, it is only one of the factors influencing some of the elementary steps and should be discussed only in relation to these steps.

Activation of the olefin molecule in the first step of the reaction, consisting in the abstraction of α-hydrogen, may proceed either as a homolytic or heterolytic bond rupture. Although the homolytic rupture of C-H bond in homogeneous reaction is energetically more favourable than the heterolytic one, the latter may be rendered much easier by interaction with the surface of an oxide of acid-base properties. In the presence of lattice

oxygen ions of basic character the first step of the oxidation of e.g.
propylene could be written as

$$CH_2 = CH - CH_3 + O^{2-}/s/ \longrightarrow \left[CH_2 = CH = CH_2\right]^- + OH^-/s/ \qquad /1/$$
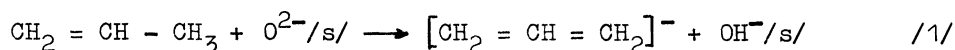
which may be considered as an acid-base reaction. As however shown by quantum-
chemical calculations /19/ discussed above, the electron transfer from the
adsorbed allyl to the metal cation of the catalyst lattice rendering the
allyl species positive must take place before this species can react further
with the lattice oxygen. A second process must thus occur, which can be
described by the equation:

$$\left[CH_2 = CH = CH_2\right]^- + Me^{+n} \longrightarrow \left[CH_2 = CH = CH_2\right]^+ + Me^{+/n-2/} \qquad /2/$$
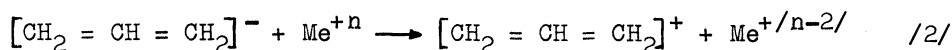
This is a pure redox process. The catalyst, in order to activate the hydro-
carbon molecule for further oxidative transformation, must thus be able to
perform both functions. It is obvious that the two stages may proceed as one
concerted reaction of mixed redox acid-base character. When comparing samples
of the same catalytic system, characterized by a given redox potential,
but differing in acid-base properties due to appropriate additions, a corre-
lation may be observed between the catalytic activity and acidity as descri-
bed by Ai /26/ for the case of $Bi_2O_3-MoO_3-P_2O_5$ system of different P_2O_5
content. On the other hand, in comparing different catalytic systems,
the differences in their redox properties may well be of much greater
significance than those in acid-base character.

The second step in the selective oxidation consists in the nucleo-
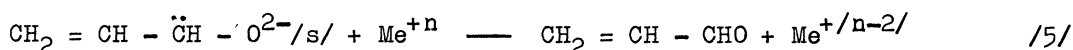philic addition of lattice oxygen ion to the allyl species:

$$\left[CH_2 = CH = CH_2\right]^+ + O^{2-}/s/ \relbar\joinrel\relbar CH_2 = CH - CH_2 - O^-/s/ \qquad /3/$$
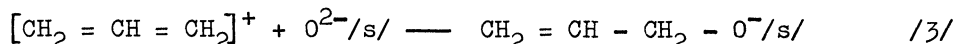
In terms of the Guttmann definition it is an acid-base process with O^{2-}
transfer. As, however, insertion of oxygen is performed by very few oxides
(although many others are known of similar acidity) it seems more plausible
to assume that some other properties of the oxide lattice beside the basicity
of the oxide ions must be responsible for its ability to insert oxygen into
an organic molecule.

Decomposition of the surface complex with desorption of acrolein may
also be considered to proceed in two states, of which one is of acid-base
character:

$$CH_2 = CH - CH_2 - O^-/s/ + O^{2-}/s/ \relbar\joinrel\relbar CH_2 = CH - \overset{..}{C}H - O^{2-}/s/ + OH^-/s/ \quad /4/$$
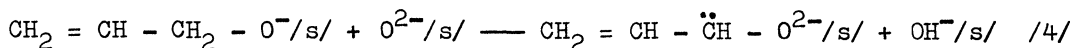
and the second of redox character:

$$CH_2 = CH - \overset{..}{C}H - O^{2-}/s/ + Me^{+n} \relbar\joinrel\relbar CH_2 = CH - CHO + Me^{+/n-2/} \qquad /5/$$

Let us now pass to the discussion of the mechanism of the third step
of partial oxidation, consisting in the oxidation of the aldehyde to the
acid. Comparison of the literature and patent data shows that on some cata-
lysts such as bismuth molybdate or tin antimonate only acrolein is formed as
the result of the oxidation of propylene, whereas with other catalysts, e.g.
cobalt and nickel molybdate, acrolein and acrylic acid are obtained in
different proportions depending on the conditions of the experiment. The
ability to transform the aldehyde into an acid seems to be a more general
property as indicated by the data of Table 4, in which results /27/ are
summarized concerning the selectivity of the same catalysts in the oxidation

of o-xylene. On catalysts, which oxidize propylene only to acrolein, o-xylene is oxidized only to toluylaldehyde, whereas phthalic anhydride is formed only with those catalysts, on which acrylic acid appears as the result of the oxidation of propylene. Thus, it may be concluded that a special type of active center must be present at the surface of the catalyst, which has the ability to transform the aldehyde group into the carboxylic group irrespective of the type of the organic molecule.

It is well known that cobalt compounds are very effective catalysts in both homogeneous and heterogeneous oxidation of aldehydes to acids. In homogeneous reactions complexes of Co^{+3} ions with oxygenated organic ligands are used as catalysts, in which Co-ion is surrounded by an octahedron of oxygen atoms. It has been postulated /28/ that the role of Co^{+3} complex consists in the generation of radicals according to the equation:

$$CH_2 = CH - CHO + Co^{+3} \longrightarrow CH_2 = CH - \overset{\bullet}{C}O + Co^{+2} + H^+ \qquad /6/$$
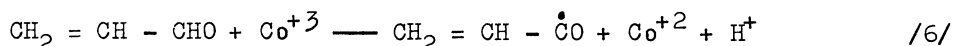
These radicals them react with oxygen to give the superacid radicals, which transform into superacid molecules. Acceleration of their decomposition is the second function of Co-complexes.

In the heterogeneous oxidation of acrolein, carried out at much higher temperatures, cobalt molybdate has been found to be active and selective catalyst. Similarly as homogeneous catalysts they contain cobalt ions directly linked to oxygen ions in an octahedral arrangement.

Many experimental data seem to indicate, that in the step acrolein — acrylic acid on cobalt molybdate catalysts it is the surface cobalt ion which

TABLE 4. Oxidation of o-xylene on olefin oxidation catalysts /27/

Catalyst	Temp. °C	Conv. %	Selectivity, %		
			tolualdehyde	phthalic anh.	CO_2
$Bi_2Mo_2O_9$	370	5.5	45.4	–	52.8
	430	35.0	33.7	–	54.3
	470	49.5	29.9	–	52.9
Bi_2MoO_6	370	18.5	45.4	–	45.9
	430	52.5	34.7	–	54.5
	470	71.7	25.6	tr.	58.0
Sn–Sb–0	390	7.5	45.3	–	49.3
(Sn/Sb=1/4)	450	21.0	34.0	–	54.8
	490	42.0	24.0	–	70.2
$CoMoO_4$	390	30.0	12.0	10.6	60.0
	410	56.0	5.2	26.4	57.0
	450	94.0	tr.	36.4	48.0
	470	98.0	tr.	31.2	48.0
$NiMoO_4$	370	40,0	6.8	13.0	62.8
	390	76.0	2.5	19.5	71.0
	410	93.0	1.0	29.0	62.4
	450	99.0	tr.	25.2	56.0
MoO_3	450	15.0	50.0	3.3	32.7
	490	30.5	51.1	2.3	30.8
V_2O_5–TiO_2	350	29.0	14.5	34.8	32.4
(V/Ti=1/2)	370	65.0	7.1	49.2	21.4
	390	99.0	–	64.5	27.6

is involved as active center. The molecular mechanism of the catalytic
action of cobalt ions, linked to oxygens in octahedral coordination must
thus account for the possibility of both processes, depending on the proper-
ties of the coordination sphere of cobalt ions /isolated complex or complex
constituting an element of crystal lattice/ as well as on conditions of
experiment /temperature and the presence of solvent molecules/.

The information on the type of bonding of acrolein in the interme-
diate complex may be obtained from the infrared spectra of acrolein adsorbed
at the surface of the cobalt molybdate catalyst adsorbed on MgO with a large
surface /fig.3/ /29/. Appearance of the new absorption bands at 1660 cm^{-1}
and 1310 cm^{-1} after heating at $200^{o}C$ indicates that the aldehyde group has
been bonded to a surface oxygen ion forming the carboxylate anion. The pre-
sence of the band at 1500 cm^{-1} may be interpreted as due to a considerable
weakening of the double bond, hinting to its interaction with the surface
metal ions. A model of the surface intermediate complex may thus be formu-
lated /30/, in which acrolein as the sixth ligand is coordinated to the
surface cobalt ion by the double bond, the aldehyde group interacting with
the surface oxygen ion forming the octahedral surrounding of the cation
/fig.4/. This model was taken as the basis for quantum-chemical calculations
of the electron distribution and energy, carried out by the semiempirical
SINDO method. Analysis of the results of calculations led to the conclusion
/30/ that a strong interaction exists between hydrogen atom of the aldehyde
group and nearest oxygen atom of the complex, resulting in considerable
weakening of the C-H bond. A transformation may thus occur consisting in the
transfer of proton to oxygen with the heterolytic rupture of C-H bond,
accompanied by a rearrangement of electrons resulting in the homolytic
rupture of bond between the vinyl group and Co-ion. Such transformation is
equivalent to reaction /6/ postulated to be the initiation of the cataly-
tic homogeneous oxidation.

Results indicate that there is a strong interaction of the planar
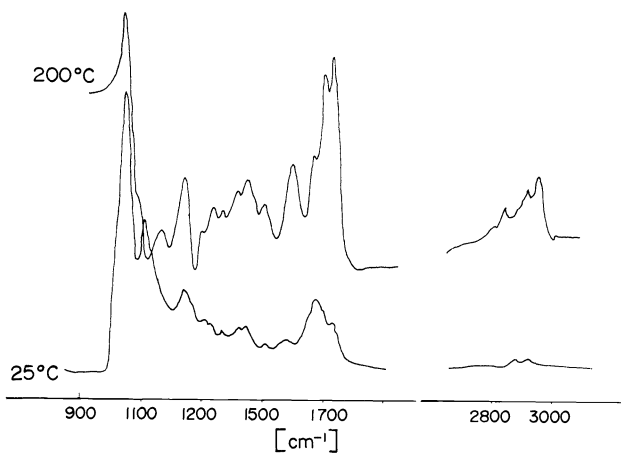oxygen of the complex not only with hydrogen but also with carbon of the

Fig.3. Infrared spectra of acrolein adsorbed on $CoMoO_{4}/MgO$
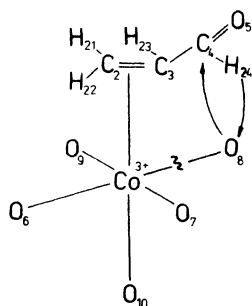catalyst at $20^{o}C$ and $200^{o}C$. /29/

Fig.4. Concerted mechanism of the oxidation of acrolein
to acrylic acid on cobalt complex. /30/

aldehyde group, resulting in simultaneous weakening of the Co-O bond, as
indicated in Fig. 4. At elevated temperature of the heterogeneous process
a concerted reaction may now occur, consisting in the transfer of proton
from carbon to oxygen, formation of the bond between oxygen and carbon and
rupture of Co-O bond, provided lattice oxygen of the catalyst is enough
mobile. This may be the case in the molybdate structures in which easy
transformation of the lattice from corner-linked octahedra into an edge-
linked arrangement makes abstraction of oxygen very facile. Such concerted
reaction may be considered as equivalent to the insertion of oxygen into
the C-H bond of the aldehyde group.

The existence of different active centers, at which the gives series
of consecutive elementary steps may proceed resulting in the formation of a
given product is the condition necessary but not sufficient for a catalyst
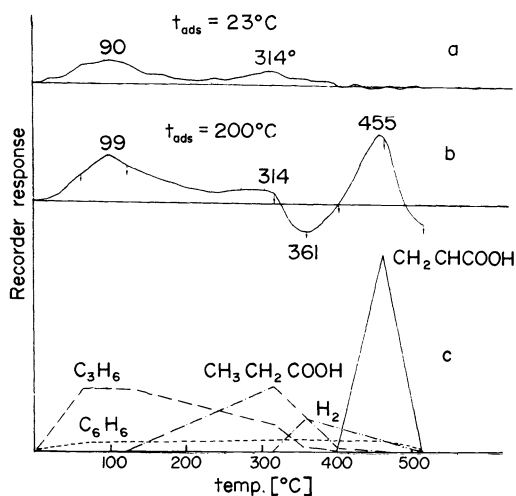to be effective. The product must be also readily desorbed from the surface.

Fig.5. Thermoprogrammed desorption from the surface of $CoMoO_4$
after preadsorption of propylene /31/ at: a/ $25^\circ C$, b/ $200^\circ C$,
c/ results of the analysis of products desorbed at $200^\circ C$.

In the oxidation of propylene to acrolein this is the case with such cata-
lysts as bismuth molybdate or MoO_3, which in the conditions of the catalytic
reaction practically do not adsorb acrolein. In the case of pure stoichio-
metric cobalt molybdate, acrolein is adsorbed irreversibly /31/. Thermode-
sorption experiments indicate /31/ that after contacting cobalt molybdate
with propylene at 250°C, no acrolein can be detected in the products of
desorption, but above 400°C acrylic acid comes off from the surface /fig.5/.
This indicates that at the surface of cobalt molybdate propylene is easily
oxidized to acrolein but the desorption rate of acrolein as the intermediate
product is(in the conditions of thermodesorption experiment)negligible in
comparison with the rate of its transformation into the carboxylate-like
complex by interaction with the next lattice oxygen ion. This complex decom-
poses with the desorption of acid only when the surface is fully oxidized.
As soon however as it becomes reduced in the conditions of the reaction, the
strength of bonding of the complex with the surface increases, as manifested
by considerable increase of adsorption of acrolein on reduction /31/.
Decarboxylation of the surface complex takes then place, resulting in the
deposition of coke according to the reaction

$$CH_2CHCOO/s/ \longrightarrow - CH_2 - CH_2 - /s/ + CO_2 /gas/ \qquad /7/$$
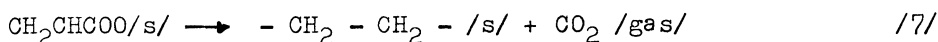
Taking into account that oxygen atoms in the carboxylate complex are surface
oxygens of the molybdate lattice, decarboxylation of this complex results in
the formation of oxygen vacancies, equivalent to the reduction of the solid
and deposition of the organic residue. The ratio of the rate of reduction of
the solid with propylene, v_r, to the rate of coke deposition, v_c, should thus
be constant irrespective of the conditions of experiment. This is indeed
the case as shown by the results of the measurements of reduction of cobalt
molybdate in propylene and acrolein /32/ summarized in Table 5.

The mechanism of the decarboxylation of carboxylate complexes at the
surface of $CoMoO_4$ was confirmed by the electron spectroscopy /33/. As an
example, fig.6. shows the spectra recorded in the course of transformations
of acrolein at the surface of $CoMoO_4$.

Table 5. Carbonization of the $CoMoO_4$ samples in the course
of the reduction /32/

Reducing gas	Temperature °C	Degree of reduction %	Oxygen consumption mol . 10^4	Amount of CO_2 formed mol . 10^4	H : C	v_c/v_r
	470	37.5	2.88	1.37	1.86	0.68
Propene	500	16.6	1.35	0.79	0.6	0.71
		48.0	3.58	1.58	2.3	0.66
		64.0	5.03	1.57	2.2	0.63
		91.5	5.85	2.06	2.3	0.85
	530	39.7	2.58	1.20	1.88	0.65
Acrolein	500	20–80	–	–	–	0.71
Propion-aldehyde	500	15–65	–	–	–	0.43

Spectrum 1 of initial sample shows the Mo3d doublet at 235.4 and
238.4 eV, and the O1s peak at 533.2 eV. Small carbon residue shows up in
form of the C1s signal at 287.6 eV. After adsorption of acrolein at liquid
nitrogen temperature /Spectrum 2/ the Mo3d and O1s peaks of the solid
disappeared indicating total coverage of the surface with the adsorbed layer
thick enough to give a spectrum, which could be considered as characteristic
of the adsorbate. It reveals the presence of two C1s peaks at 285.1 and
288.0 eV, their intensity ratio being approximately 2:1. They may thus be
interpreted as related to the two different carbon atoms in acrolein. The
effective charge on carbon atom in aldehyde group is more positive than the
charge of atoms of the vinyl group , and the B.E. value of C1s electrons is
higher. The position of carbonyl oxygen amounts to 532.8 eV. On heating to
room temperature carbonyl carbon peak dissapears, whereas that of vinyl
group shifts to 286.8 eV and its intensity considerably increases /Spec-
trum 3/. Simultaneously the O1s peak shifts at first to 534.3 eV and then
starts to decrease in intensity as lattice O1s peak at 532.6 eV
reappears indicating that the transformations of species in the
chemisorbed layer are now being observed. Apparently two processes have
taken place in the course of heating. The vinyl carbon peak shifted to
higher B.E. and assumed the value similar to that of C1s electrons of para-
ffinic chain carbons, observed after adsorption of propionic acid. This may
be explained by assuming that polymerisation of acrolein took place and the
vinyl carbons disappeared as the result of the formation of paraffinic
chains. A second process must be responsible for the shift of the B.E. of
oxygen to higher value,close to that of oxygen in adsorbed carboxyl group,
in which oxygen atom has a more positive effective charge. We may thus
assume that the aldehyde group of acrolein has reacted with the lattice
surface oxygen ion forming the chemisorbed carboxyl group.

After outgassing the sample for two hours at 593°K the O1s peak at
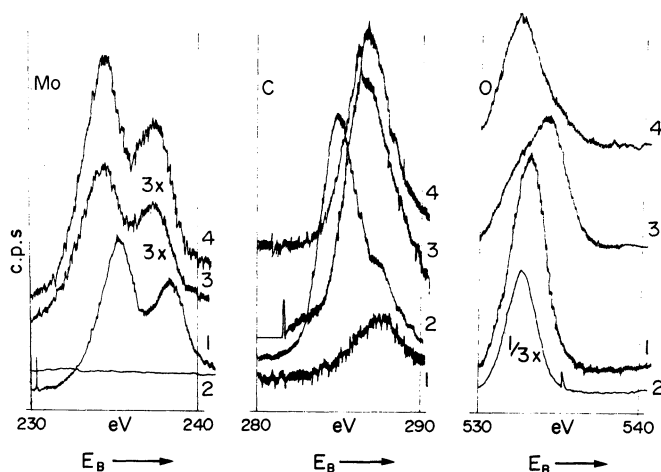534.3 eV related to carboxyl groups disappeared completely /Spectrum 4/,

Fig.6. ESCA spectra of Mo3d, C1s and O1s electrons in the
course of transformations of acrolein on CoMoO$_4$, 1 - initial
sample, 2 - after adsorption at 77°K, 3 - after desorption
at 298°K, 4 - after outgassing at 593°K for 1.5 hr. /33/

whereas the intensity of C1s peak practically did not decrease. This indica-
tes that decarboxylation of the oxygenated hydrocarbon species took place on
heating, leaving at the surface a deposit of polymerised chains. The spec-
trum remained unchanged after contacting the sample with 0.1 Tr of oxygen
for 0.5 hr at $523^{o}K$, however, in comparison with the initial sample, the
intensity of Mo3d, Co2p and lattice O1s peaks was about 50 % lower confir-
ming the presence of strongly chemisorbed species.

When discussing the properties of an active catalyst it should be
borne in mind that all functions mentioned until now as requirement for
selective oxidation are necessary but not sufficient.

After the given elementary step of the catalytic reaction has taken
place with the participation of lattice oxygen and formation of oxygen va-
cancy the active center at the surface is left in the reduced state. Before
such elementary step can be repeated, the active center must be
reoxidised. This reoxidation can be realised in three ways, as shown in
Fig. 7: by incorporation of oxygen from the gas phase /I/, by diffusion of
oxygen ions from the bulk /II/ and by the diffusion of the reduced lattice
constituents to the nuclei of the new phase of reduced solid and exposition
of the underlying fresh crystal planes /III/. Depending on the rate of such
regeneration of the active center, its "dead time" may be shorter or longer.
In the case of such lattices as bismuth molybdate the mobility of lattice
oxygen is very high and process /II/ operates very effectively. In such
conditions the "dead time" of active centers is very short, the turn-over
number on these centers is very large and the catalyst shows high activity.
This process of regeneration does not however operate in cobalt molybdate.
When oxygen is present in the gas phase, regeneration of active centers
takes place by path /I/ whereas in the absence of gaseous oxygen only path
/III/ remains for regeneration. As however the rate of nucleation of reduced
phases, which in this case are cobalt molybdite and cobalt-molybdenum /IV/ -
spinel /34/ ; and of their growth is very low at the temperature of the
calaytic reaction, the activity of the cobalt molybdate drops in the absence of
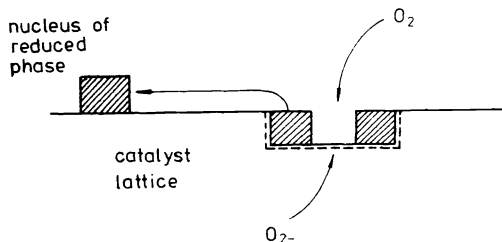gaseous oxygen to a very low value.

Fig.7. Mechanism of the regeneration of an active center at
the surface of oxide catalysts. I — by reoxidation with
gaseous oxygen, II — by diffusion of lattice oxygen ions,
III — by nucleation of the reduced phase and exposition of
a new lattice plane.

The question may now be raised as to which parameters of the solid
are responsible for the very high mobility of oxygen in bismuth molybdate
as opposed to cobalt or nickel molybdate. Studies of the mechanism of the
reduction of group VIb transition metal oxides have led in recent years to
the discovery of the phenomenon of crystallographic shear. Removal of oxygen
ions from the lattice of these oxides results in the formation of ordered
arrays of oxygen vacancies, followed by a very facile rearrangement of the
layers of initially corner-linked metal-oxygen octahedra into an arrangement
of edge-linked octahedra, resulting in the formation of a shear plane. This
is shown in Fig.8. It was recently suggested /35/ that this process may be
responsible for a very rapid transport of oxygen observed in lattices of such
oxides as compared with the diffusion of oxygen in closepacked structures of
the majority of transition metal oxides. On the other hand we would like to
point out that the easy evolution of one oxygen ion in the transformation
from corner-linked to edge-linked arrangement of $Mo-O$ octahedra may be one
of the factors creating the ability of these structures to insert oxygen
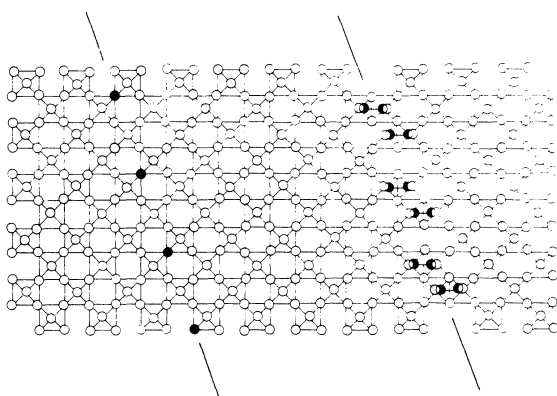into the organic molecule in processes of selective oxidation of hydro-
carbons.

Fig.8. Formation of a shear plane in WO_3 structure.
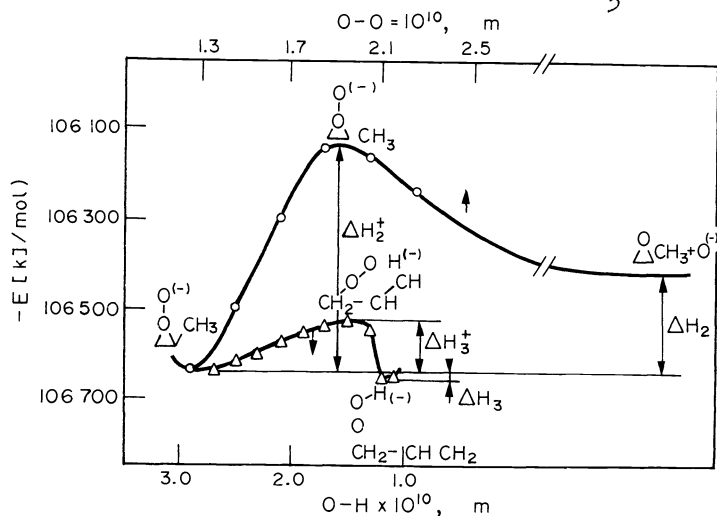

Fig.9. Total MINDO/2 energies plotted against the 0-0
distance and the 0-H distance. /40/

Interesting informations on the changes of the bond structure accompanying the formation of shear planes in various stages of the reduction of group VA, VIA and VIIA metal oxides and its bearing upon the mechanism of the reduction of their more complex compounds as oxysalts were quite recently obtained by photoelectron spectroscopy /36,37,38/.

When discussing the selectivity of catalytic reactions it should always be borne in mind that even when the same intermediate complex is formed at the same active center of the catalyst surface, different reaction paths may be followed depending on the structure of the reacting molecule. Introduction of a new functional group into the organic molecule may namely influence,by the inductive or mesomeric effect,the reactivity of the intermediate complex to such an extent that the mechanism of its transformation is completely changed. Oxidation of ethylene to ethylene oxide on silver catalysts may serve as an example. As shown by Sachtler et al /39/ the role of silver consists in the activation of the oxygen molecule into a superoxide ion O_2^-, which then reacts with ethylene to form ethylene oxide with simultaneous splitting of the O-O bond. Recently Zahradnik et al /40/,using the MINDO/2 quantum chemical calculations of the changes of the potential energy along the reaction coordinates,have demonstrated that when one of the hydrogen atoms in ethylene is substituted by the methyl group, i.e. propylene is used instead of ethylene, a new reaction path leading to propylene peroxide appears, characterized by a much lower potential barrier than the reaction path to propylene oxide /Fig.9/. This is an elegant explanation of the observation that on silver catalysts propylene forms the total oxidation products whereas ethylene is oxidized selectively to ethylene oxide.

Results of our discussion are summarized in Fig.10. When oxygen is activated at the surface of the catalyst, ionic radical oxygen species O^- and O_2^- are formed which show very high activity in catalytic reactions and are the main oxidizing species in the total oxidation of simple molecules such as H_2, CO, CH_4 etc. They may be considered as electrophilic reagents,
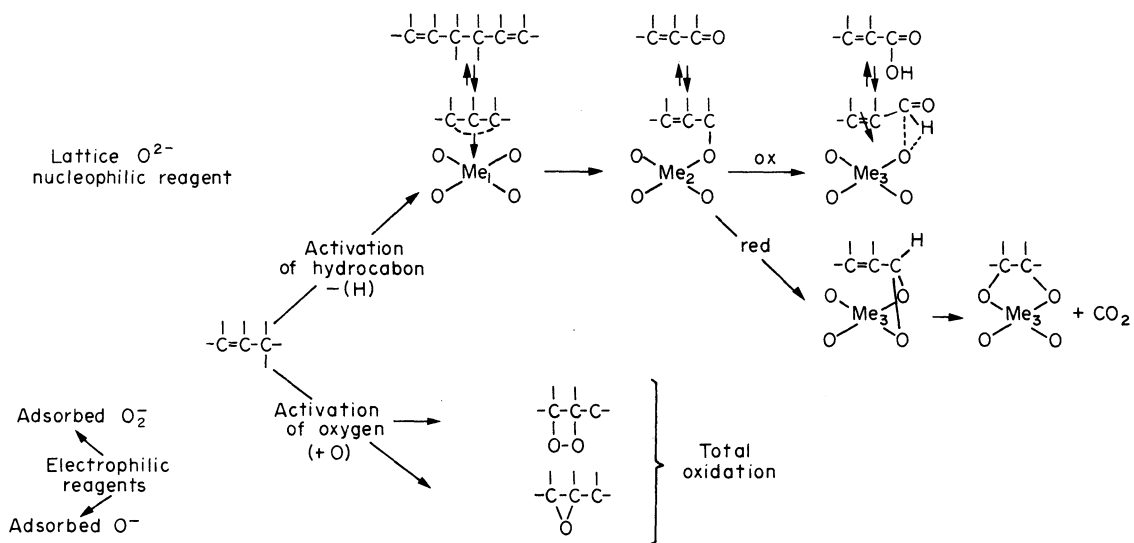

Fig.10. Mechanism of the oxidation of hydrocarbons.

which in reactions with olefins attack the molecule in the regions of highest electron density. Such electrophilic addition of O_2^- or O^- results in the formation of peroxy- or epoxy- complexes, respectively, which in the conditions of heterogeneous catalytic oxidation are intermediates of the degradation of the carbon skeleton and total oxidation.

When hydrocarbon molecule is activated, a different reaction path is initiated, consisting in the series of consecutive oxidative steps, each of them requiring different active centers to be present at the catalyst surface. The type of product obtained depends thus on the type and mutual proportions of these centers, as well as on the ratio of the rate of desorption of the particular intermediate complex to the rate of its transformation into the intermediate complex next in the series. This rate may strongly depend on the degree of reduction of the surface, attained in the course of the reaction, as it is the case with the carboxylate complex. On oxidized surface this complex desorbs in the form of acid, whereas on reduced surface it undergoes the decarboxylation, resulting in the deposition of coke. It should be emphasized that in the reaction path of partial oxidation it is the cations of the catalyst which act as oxidizing agents in one of the consecutive steps of the series, forming electrophilic hydrocarbon species. The lattice oxygen ions are nucleophilic reagents which have no oxidizing properties. They are inserted into the activated hydrocarbon molecule by nucleophilic addition, forming an oxygenated product, which after desorption leaves an oxygen vacancy at the surface of the catalyst. Such vacancies are then filled with oxygen from the gas phase, reoxidizing simultaneously the reduced cations.

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