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The improvement of oxidation catalysts

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ABSTRACT. The mechanism of the action of additives introduced into oxide catalysts and silver to increase their activity and selectivity in the oxidation of various organic substances has been examined. Additives can change the kinetic parameters of a process (the rate and activation energy of the reaction) and influence the reaction mechanism by their effect on the structure of the surface compounds and on the energy of the bonds which they form with the surface. The modification of the catalysts gives new compounds (both in the bulk and on the surface), leading to the production of new active centres. The action of additives introduced into multicomponent oxide catalytic systems, and various aspects of their modification by acidic and alkaline additives, have been discussed.

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I. Introduction

The efficiency of catalysts is determined by two parameters—the degree of conversion of the starting materials and the selectivity of their conversion into the required products. One of the principal methods for controlling these parameters is by introducing various additives into the catalyst.

Previously, on the basis of the chemical properties of the materials, two types of additive were distinguished: promoters, which increase the activity of catalysts, and poisons, which decrease the activity.[1]

In the period 1940–1950, the study of the extensive oxidation of hydrocarbons on various oxide catalysts and platinum revealed a new phenomenon: the same additive, introduced into a catalyst, may have a promoting or a poisoning effect on the activity of the catalyst, depending on its concentration in the solid.[2–4] It was suggested that the effect ot additives on the properties of catalysts should be described as their modification. The two-fold action of additives was attributed to the change in the same sense in the activation energy and the pre-exponential factor (Fig. 1). This led to an extremal dependence of the reaction rate on the additive concentration (Fig. 2). The phenomenon of catalyst modification was found to be characteristic of not only extensive but also partial oxidation.[5,6] Thus the introduction of additives into copper oxide CuO, a catalyst for the oxidation of propylene to acrolein, brings about the change in the rate and activation energy of formation of the products characteristic of modification. When lithium ions are added to copper oxide, the energy of formation of acrolein changes from 12 kcal mol^{-1} to 22 kcal mol^{-1}, and that of CO_2 from 26 kcal mol^{-1} to 16 kcal mol^{-1}. The pre-exponential factor increases regularly in the order CuO + Li < CuO + PO_4^{3-} < CuO < CuO + Sb^{3+}, from 10^{17} to 10^{22}.

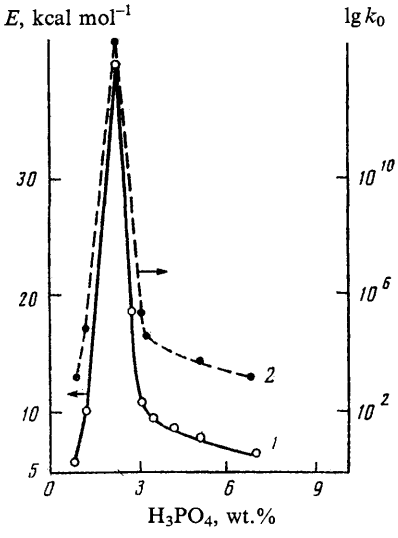


Figure 1. The influence of added H_3PO_4 on the activity of the $MgCr_2O_4$ catalyst in the extensive oxidation of iso-octane: *1*, change in the activation energy; *2*, change in the pre-exponential factor.[3]

Further studies of the control of the conversion and selectivity of oxidation processes showed, however, that these explanations are inadequate. Additives may react with the basic catalyst matrix to form solid solutions and new compounds, and hence increase the number of phases in the catalyst. The effect of these impurities is not limited to changing the phase composition of the catalyst; as a result of the change in the structure, they also influence the probability of electron transitions between the elements in the solid. The rearrangement of the catalyst structure, leading to changes in

the bulk characteristics, also lead to changes in the surface; the additives also take part in the production of the active centres on which the catalytic reaction takes place.

The introduction of additives has produced highly selective catalytic systems used in industry, but the additives have been selected empirically, since the multifunctional character of their action makes it difficult to determine the basic principles of the selection of modifiers for increasing the efficiency of catalysts.

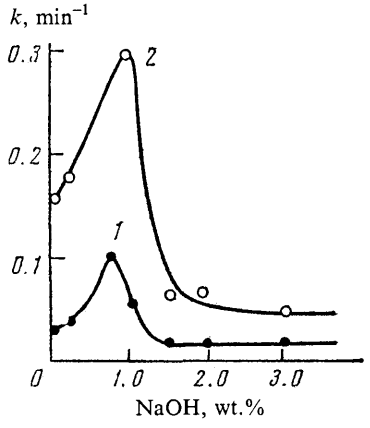


Figure 2. Influence of added NaOH on the rate constant of the oxidation of iso-octane on tungsten oxide at 320 °C (*1*) and 420 °C (*2*).[4]

The accumulated experimental data on modification have not been fully reviewed. A review[8] was published in 1987, dealing with the promotion of various metallic and oxide catalysts for the Fischer–Tropsch synthesis, the hydrogenation of CO, etc., but the nature of the modifying action of the additives introduced into a large number of oxidation catalysts was not examined systematically.

Attempts have been made to explain the mechanism of the modification of catalysts using various theories of catalysis. In the period 1950–1960, Vol'kenshtein,[9] who developed the electronic theory of catalysis, explained the mechanism of the modification of semiconducting oxide catalysts in terms of the band model, attributing it to a change in the position of the Fermi level in the crystals. According to these ideas, additives can change the electronic properties of the crystal in the bulk and on the surface. The catalytic activity of specimens should therefore be compared with the electronic characteristics of the solid, for example the electrical conductivity or the work function. The introduction of donor or acceptor additives changes the position of the Fermi level and decreases the degree of coverage of the catalyst surface by the reagents, which become charged on adsorption (electron acceptors or donors), and this may even lead to a change in the limiting stage of the process and its rate. A large number of papers have been published on the relationship between the electrical conductivity and the work function in the oxidation of various substances on oxide semiconductors.[5] The sign of the charge on a given impurity may be different in the bulk and on the surface of an oxide, however. The electronic characteristics of the impurities in a solid and their influence on a reaction rate may be different, depending on their distribution. It is therefore impossible to establish the mechanism of the varied action of additives by examining only the electronic properties of semiconducting oxides.

In the case of metals, it is considered that the additives and reagents on their surface form charged dipoles, whose electrostatic interaction changes the degree of covering of the surface by the reagents and hence influences the reaction rate.

The study of the modification of silver by additives which are electron donors or acceptors has shown,[5] however, that the mechanism of action of these additives cannot be explained entirely in terms of the interaction of dipoles. The change in the work function when silver is modified cannot be responsible for the change in the activity of the catalyst or the selectivity of the process, and is only an "indicator" of the change in the properties of the surface of the solid. When potassium or halogen ions are introduced into silver, the additive migrates into the bulk, dissolving in its lattice with the formation of microcrystals. The change in the work function is merely a reflection of these processes, and cannot influence the selectivity of catalytic reactions.[10,11]

To determine the mechanism of the action of additives on the properties of catalysts, it is necessary first to study their structure and phase composition, the mobility of oxygen in them, and their acid–base properties.

Of the large number of modified catalysts, various simple and complex oxide systems and one metallic catalyst, namely silver, are examined in the present review.

II. The influence of additives on the structure and phase composition of catalysts

1. Simple metal oxides

Additives are introduced into catalysts in different ways: during the preparation of the basic matrix or by adsorption on the surface of a prepared catalyst. Depending on the method of introduction, the additives may be distributed in different ways in the bulk of the catalyst and on its surface. This may lead to variations in phase composition, which are examined here for the case of a vanadium oxide catalyst.

As a consequence of the characteristics of its structure, vanadium pentoxide reacts readily with foreign metal ions to give vanadium bronzes, that is non-stoichiometric double oxides with the general formula A_xBO_3, showing characteristic semiconducting or metallic conductivity.[12,13] The formation of bronzes can be described as the result of the introduction of foreign atoms or ions into the main lattice. The metal A, entering the lattice, occupies some of the free sites and has no influence on the structure of the main oxide. The introduction of A leads to the production of an impurity level in the band gap of BO_3 below the conductivity band or in the actual band, which is "populated" by electrons of the metal A. Vanadium bronzes are formed particularly readily with the alkali metals and silver. In addition, for the oxidation of aromatic hydrocarbons to aldehydes, use is made of vanadium–molybdenum oxide systems consisting of a solid solution of MoO_3 in V_2O_5 (V : Mo = 1 : 0.27) containing added silver and copper ions. The study of these catalysts by X-ray diffraction, infrared spectroscopy, and EPR has detected the formation of bronzes with vanadium ions in different arrangements. The production of these structures leads to a change in the rate of oxidation of hydrocarbons. According to Volkov and Novak,[13] the diffusion coefficient of oxygen, which is 10^{-8} cm^2 s^{-1} in

V_2O_5, is lower by a factor of 10^2 in the bronzes, due to the presence in the structure of the latter of cavities through which oxygen, the principal component of oxidation processes, moves readily.

To obtain effective oxidation catalysts, vanadium pentoxide is added in different concentrations to MoO_3 and other oxides; the catalytic activity and selectivity depend significantly on the vanadium concentration in the specimen.

According to Andrushkevich and Kuznetsova,[14] the active component of the vanadium–molybdenum oxide catalyst for the oxidation of acrolein to acrylic acid is the compound VMo_3O_{11}, whose maximum concentration in this system is reached at a V_2O_5 concentration of 7–15 mol%; the compounds VMo_2O_{8+x} and $V_6Mo_4O_{25}$ are also formed. Other additives are also frequently introduced into these systems. An effective additive to the vanadium–molybdenum catalyst for the synthesis of acrylic acid is copper oxide.[15] The introduction of the Cu ion gives a V–Mo–Cu oxide compound of variable composition, shown by X-ray diffraction, X-ray photoelectron spectroscopy, and infrared spectroscopy to be based on the structures of VMo_3O_{11} and VMo_2O_{3+x}.

The V_2O_5–MoO_3 system is an active catalyst for the oxidation of benzene to maleic anhydride. It contains the new compound $V_9Mo_8O_{40}$, and also V^{4+} ions, whose maximum concentration, according to EPR data,[16] corresponds to the limiting solubility of MoO_3 in V_2O_5 (about 30 mol%).

A vanadium–titanium oxide catalyst is used for oxidising *o*-xylene to phthalic anhydride.[17] The highest rate of formation of phthalic anhydride and the highest selectivity are observed when 2.5–8 mol% V_2O_5 is introduced into inactive titanium dioxide. Vanadium ions coordinated to titanium ions, and the compound V_6O_{13}, are formed in this system. EXAFS has shown[18] that titanium dioxide brings about disordering of the V_2O_5 structure.

Another example of the action of a modifier on the phase composition of a simple oxide catalyst is provided by the use of MoO_3 as additive. X-Ray diffraction and infrared and ultraviolet spectroscopy[19] have shown that when MoO_3 is introduced into inactive tin dioxide SnO_2 in the ratio Sn : Mo = 9 : 1, a solid solution of MoO_3 in SnO_2, and also Mo and Sn oxides, are detected in the system. This catalyst is used to oxidise propylene to acetone.

The rate of formation of acetone shows an extremal dependence on the concentration of Mo ions in SnO_2; the rate decreases when the Mo concentration is higher than that corresponding to the optimum ratio Sn : Mo = 9 : 1.

Thus the modification of simple oxides by various additives gives new catalytic systems consisting of solid solutions, new compounds, and microheterogeneous formations, with structures and phase compositions differing from those of the simple oxides.

2. Complex metal oxides

Multicomponent mixed oxide systems are highly effective catalysts for the selective oxidation of alkenes.

Bismuth and cobalt molybdates are most frequently used for the oxidation of propylene to acrolein. The vanadium–molybdenum oxide system is used to convert aromatic hydrocarbons into acid anhydrides, and vanadium–phosphorus catalysts are used to oxidise butane to maleic anhydride. The introduction of various additives into these systems increases their efficiency.

The addition of iron to bismuth molybdate gives a complex oxide system containing the triple oxide $Bi_2Fe_2Mo_2O_{12}$ and Bi and Fe molybdates. Table 1 gives data on the influence of the modification of the catalyst by iron on the rate and selectivity of the formation of acrolein from propylene.[20] The individual triple compound $Bi_2Fe_2Mo_2O_{12}$ has a low activity, and its catalytic properties are similar to those of bismuth molybdate. The modification of $CoMoO_4$ by Bi, Fe, and Sb additives leads to a sharp change in its catalytic properties in the oxidation of propylene to acrolein. The X-ray diffraction study of these systems[21] has shown that new compounds are formed (Table 2).

Table 1. Influence of the Fe ion on the activity and selectivity of the Bi–Mo catalyst.

Fe^{3+} concentration, at.%	Phase composition	Rate of formation of acrolein at 340 °C, ml m^{-2} min^{-1}	Selectivity with respect to acrolein, %
0	$Bi_2(MoO_4)_3$	0.44	88
2	$Bi_2(MoO_4)_3$, $Fe_2(MoO_4)_3$, the triple compound $Bi_2Fe_2Mo_2O_{12}$	1.32	98
14.8	$Bi_2(MoO_4)_3$, $Fe_2(MoO_4)_3$, the triple compound $Bi_2Fe_2Mo_2O_{12}$	3.75	91
33.3	the triple compound $Bi_2Fe_2Mo_2O_{12}$	0.58	87

Table 2. Modification of $CoMoO_4$.[21]

Composition of the catalyst	Phase composition
Co + Mo	α-$CoMoO_4$, β-$CoMoO_4$, MoO_3
Co + Mo + Bi	α-$CoMoO_4$, β-$CoMoO_4$, MoO_3, $Bi_2O_3 \cdot 3MoO_3$
Co + Mo + Bi + Fe	α-$CoMoO_4$, β-$CoMoO_4$, MoO_3, $Fe_2(MoO_4)_3$, $Bi_2O_3 \cdot 3MoO_3$
Co + Mo + Bi + Fe + Sb	α-$CoMoO_4$, β-$CoMoO_4$, MoO_3, $Fe_2(MoO_4)_3$, $CoSb_2O_6$, $Bi_2O_3 \cdot 3MoO_3$

The catalytic system Co–Mo–Bi–Fe–Sb–O is used for the partial oxidation of isobutylene to methylacrolein. X-Ray diffraction and Mössbauer spectroscopy[22] have been used to study the structure of this multicomponent oxide system at different concentrations of the additives Bi and Fe. In addition to the basic matrix structure of $CoMoO_4$, the catalyst also contains the molybdates of bismuth $Bi_2(MoO_4)_3$ and iron(III) $Fe_2(MoO_4)_3$, and also the complex compound $M_2FeMo_2O_{12}$, where M = Bi, Sb. Figs. 3 and 4 give the dependence of the conversion of isobutylene and the relative concentration of the phases $Fe_2(MoO_4)_3$ and $M_3FeMo_2O_{12}$ on the concentrations of Bi and Fe in the system $Co_6Mo_{12}Bi_xFe_ySbO_z$. The maximum conversion of isobutylene is achieved for $x = 1$ and $y = 4-6$, when the catalyst contains equal quantities of the two iron-containing phases.

Thus the modification of complex oxide systems, which already contain several phases and elements in different oxidation states, leads to a further increase in their complexity. These complex oxide

systems make it possible to influence different stages of the oxidation and to increase the rate and selectivity of the reaction. The use of new complex catalytic systems has made it possible to achieve almost 90% selectivity, whereas on simple oxides the selectivity does not exceed 40–50%.

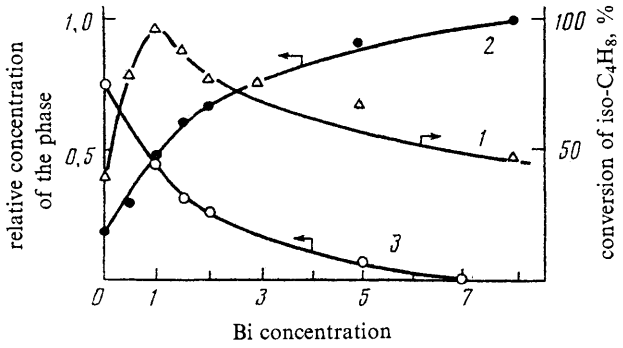


Figure 3. Dependence of the conversion of isobutylene at 370 °C (*1*) and the relative concentration of the phases $Bi_3FeMo_2O_{12}$ (*2*) and $Fe_2(MoO_4)_3$ (*3*) on the concentration of bismuth in the catalyst.[22]

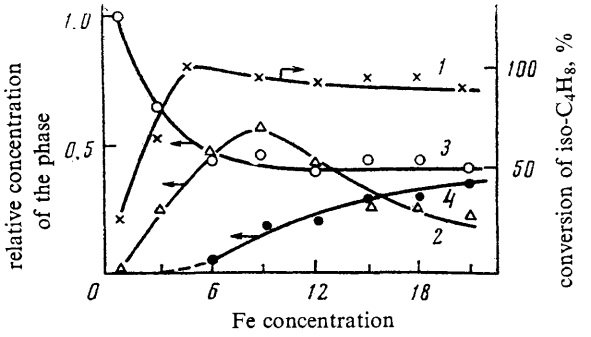


Figure 4. Dependence of the conversion of isobutylene at 370 °C (*1*) and the relative concentration of the phases $Fe_2(MoO_4)_3$ (*2*), $Bi_3FeMo_2O_{12}$ (*3*), and α-Fe_2O_3 (*4*) on the concentration of iron in the catalyst.[22]

III. The influence of additives on the state of oxygen in oxide catalysts

A large number of studies by different methods (using isotopes, reduction–reoxidation, etc.) have shown that the selective oxidation of organic substances on oxide systems involves the oxygen of the catalyst lattice.[5,23,24]

Oxidation involving the oxygen of the lattice is accompanied by the reduction of cations, which, when the process is carried out under stationary conditions, are reoxidised by the oxygen of the gas phase.

The formation of various non-stoichiometric oxides in the reduction of MoO_3 by the substance being oxidised has been examined.[24] The phase transitions do not involve extensive rearrangement of the lattice, but "crystallographic shearing" is observed,[25] that is during reduction, some of the oxygen is removed from the lattice with the production of vacancies, the distance between the Mo ions decreases, and the bonding between the oxygen octahedron around Mo is altered. The process gives blocks having a comparatively unaltered structure, separated by shear planes made up of other small blocks with a different regular structure.

In the reduction of MoO_3, the rapid movement of an electron into the bulk and its capture by Mo^{6+} ions close to a vacancy gives an Mo^{5+} ion

$$Mo_s^{6+}O_s + RH \rightarrow \left[\begin{array}{c} H \\ | \\ Mo_s^{5+}O_s \end{array}\right] R^+ \xrightarrow{Mo_v^{6+}O_v} Mo^{6+}\square\, RO + Mo_v^{5+}O_v + H^+.$$

The vacancy moves from the surface to the defect. The movement of the vacancy corresponds to the diffusion of oxygen to the surface by a mechanism involving a large number of displacements of the micro-blocks; thus the surface layer of the catalyst during the reaction is constantly rearranged, and the oxygen atoms change positions.

Table 3. Characteristics of the catalysts $Bi_{1-x/3}V_{1-x}Mo_xO_4$.[26]

x	Surface concentration of Bi, at.%	Rate of reduction by hydrogen $\times 10^{-6}$, mol min^{-1} m^{-2}	Mobility of the oxygen ions of the lattice,* %
0.00	20.6	12.1	37.0
0.09	14.6	8.7	57.4
0.21	15.1	7.8	75.1
0.27	14.6	7.6	72.2
0.45	14.0	6.4	100

*The fraction of oxygen ions of the lattice taking part in the oxidation, relative to the total quantity of oxygen ions of the lattice.

The introduction of additives into these systems influences the rate of migration of oxygen, and also the rate of rearrangement of the oxide lattice. The rates of these processes depend on the mobility of the oxygen of the solid lattice. The composition dependence of the mobility of oxygen in the $Bi_{1-x/3}V_{1-x}Mo_xO_4$ system, used to oxidise propylene to acrolein, has been studied using ^{18}O.[26] Table 3 gives the rates of the reduction by hydrogen of catalysts with different compositions, and data characterising the mobility of the lattice oxygen. The rate of reduction by hydrogen changes in the opposite sense to the change in the rate of reduction by propylene, that is the ability of the catalysts to undergo reduction is influenced strongly by the nature of the reducing agent. The dependence of the rate of reduction on the nature of the reducing agent is apparently due to the fact that the reactions of different reagents with the oxygen of the catalyst take place on different active centres. Increase in the concentration of the additive in the catalyst alters the composition of the surface, influencing the rate of its reduction and the activity.

A microcatalytic method combined with Mössbauer spectroscopy has given quantitative data on the reduction by propylene of cobalt molybdate modified by added Fe and Bi.[27] Fig. 5 gives the Mössbauer spectra (MS) of iron in the original Co–Mo–Bi–Fe oxide catalyst and in the catalyst reduced at different temperatures. In the oxidised state, Fe is present in crystalline $Fe_2(MoO_4)_3$, and the chemical shift is $\delta E_I = 0.68 \pm 0.01$ mm s^{-1}. When this catalyst is treated with propylene, partial reduction takes place to give β-$FeMoO_4$. Fig. 5 shows that the extent of the reduction, determined from the ratio of the areas of the spectra as $[Fe^{2+}]/([Fe^{2+}] + [Fe^{3+}])$, increases sharply with temperature; it has the values 0.14 at 270 °C, 0.44 at 350 °C, and 0.76 at 390 °C. These spectroscopic data were used to calculate the quantity of oxygen removed from the lattice in the reduction of $Fe_2(MoO_4)_3$ to $FeMoO_4$. The results of this calculation are compared with the data obtained in the catalytic micro-reactor in Table 4.

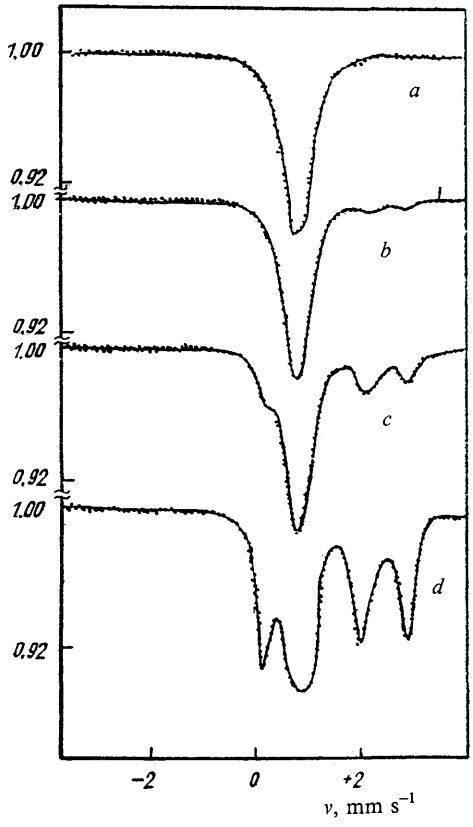


Figure 5. Mössbauer spectra of a Co–Mo–Bi–Fe catalyst before (*a*) and after its reduction by propylene at 270 (*b*), 350 (*c*), and 390 °C (*d*).[27]

Table 4 shows that almost all the oxygen removed belongs to iron molybdate. The Mössbauer spectrum of the reoxidised catalyst is identical to the original spectrum.

The liberation of the oxygen of iron(III)molybdate to give divalent iron molybdate and anion vacancies takes place according to the scheme:

$$Fe_2(MoO_4)_3 \rightarrow \{2FeMoO_4(MoO_3)\}\,\square_x + x\,[O],$$

where □ represents an anion vacancy.

The ionisation of vacancies leads to the production of an excess negative charge;[28] a redistribution of electron density takes place, affecting the entire iron molybdate crystal and leading to its reduction. Thus the modification of the Co–Mo catalyst leads to the formation of iron molybdate which "supplies" the oxygen for the selective oxidation of hydrocarbons.

Table 4. Quantity of oxygen (*n*) removed from a Co–Mo–Bi–Fe catalyst by the reaction with 40 C_3H_6 pulses.[27]

Reduction temperature, °C	10^{-19} *n*, atom g^{-1}	
	kinetic data	Mössbauer data
270	2.2	2.5
350	7.0	8.0
390	11.0	13.0

The removal of oxygen from the catalyst lattice under the influence of a hydrocarbon is accompanied by a simultaneous change in the oxidation state of the metal ions; if two additives are introduced into the catalyst, charge transfer takes place between them.

Mössbauer spectroscopy has been used to study the reactions of Fe and Te, introduced into $CoMoO_4$, with the components of the reaction mixture during the oxidation of propylene to acrolein.[29] On modification, the activity of the catalyst and the selectivity of the oxidation increase several-fold (Table 5). Spectroscopic data show that the introduction of the additives into the oxide catalyst gives new compounds $Fe_2(MoO_4)_3$ and $CoTeO_4$; reaction with the mixture leads to a partial change in the oxidation states of the Fe and Te ions.

Table 5. Influence of added Fe and Te on the activity of $CoMoO_4$ and the electronic transitions.[29]

Additive	Change in oxidation number	Conversion of C_3H_6, %	Selectivity of C_3H_4O formation, %
None	—	10	10
Fe	$Fe^{3+} \rightarrow Fe^{2+}$	63	36
Te	$Te^{6+} \rightarrow Te^{4+}$	55	30
Fe + Te	$Te^{6+} \rightarrow Te^{4+}$ $Fe^{3+} \rightarrow Fe^{2+}$	72	44

The rate of oxidation of different organic substances on V_2O_5, V_2O_5–MoO_3, and other vanadium-containing catalysts is generally proportional to the concentration of V^{4+}, which is formed during

the process as a result of redox reactions, and also under the influence of the additive. The change in the oxidation state of vanadium is accompanied by the formation of a $V^{4+}=O$ double bond; this form of oxygen is more active in selective oxidation than other forms.

The influence of added P, Mo, W, and Sn on the catalytic properties of V_2O_5 in the oxidation of benzene to maleic anhydride has been studied.[30–32] Mo ions increase the activity of the catalyst and the selectivity of the process, whereas W and P increase the selectivity but decrease the activity. The presence of Sn ions in V_2O_5 leads to the extensive oxidation of benzene. This influence of the additives on the catalytic properties was related to their electronegativities:

$$Sn^{4+} < V^{5+} < W^{6+} < P^{5+} < Mo^{6+}.$$

The introduction of the more electronegative ions (W, P, Mo) leads to a decrease in the electron density of the $V^{4+}=O$ bond, associated with charge transfer between the vanadium ions and the additive, leading to a change in the length of the $V^{4+}=O$ bond. When this bond becomes shorter, the oxygen becomes more reactive, and the catalyst becomes more effective in the oxidation of benzene.

Thus the state and reactivity of oxygen are related to the structure of the catalyst and the electron transitions in the solid. The rearrangement of the structure and the change in the rate of electron transfer under the influence of the additives are factors determining the selectivity of oxidation processes and the activity of catalysts.[28]

IV. The modification of catalysts by acidic and alkaline additives

1. Oxide systems

There is a large amount of data (see for example the published review[33]) on the action of alkaline additives in catalysts on various reactions. The trivial explanation of this phenomenon reduces to the examination of the acid–base properties of the surface of the solids and the reagents. The alkaline and acidic properties of the reaction products and the strength of their bonding with the surface[34] are regarded as factors determining the activity of the catalysts.

It has been shown for the case of the vanadium–molybdenum oxide system that the selectivity of the oxidation of benzene to maleic anhydride can be increased by introducing both alkaline (Na) and acidic (P) additives into the catalyst.[34] This increase in selectivity is probably due not to a change in the acid–base properties of the catalyst but to some other factors. EPR has shown that the presence of Na and P in the catalyst leads to an increase in the concentration of V^{4+} ions and the number of V=O bonds, and XPS has shown a change in the ratio of the ions $Mo^{6+}:V^{4+}$ in the layers next to the surface.

When the ions Na, K, Rb, and Cs were introduced into the vanadium–titanium catalyst for oxidising *o*-xylene to phthalic anhydride (PA),[35] the selectivity of the process increased and reached 87%, as a result of a decrease in the rate of the more extensive oxidation of PA. The selectivity of the formation of PA increases with increase in the electronegativity of the alkali metal ions. All the alkaline elements added to the catalyst keep the vanadium in the vanadium–titanium oxide catalyst in the stable oxidation state, and simultaneously neutralise the acidic centres of the surface.

The introduction of the K ion into the Sn–Mo–Fe catalyst for the oxidation of propylene to acetone increases the selectivity from 23% to 94% by decreasing the rate of more extensive oxidation. The presence of the K ion leads to an increase in the concentration of the reduced form of Mo produced by reaction with propylene.

The influence of alkali metals (Li, Na, K) and alkaline earth metals (Mg, Ca, Ba) on the properties of the unique vanadium–phosphorus catalyst for the oxidation of butane to maleic anhydride has been studied.[36] No relationship between the acidic properties of the surface and the rate of oxidation of butane was detected, but a change in the bond energy of oxygen in the lattice and in the catalytic properties on modification was observed.

The mechanism of the action of alkaline additives has been studied in more detail for the Co–Mo–Bi–Fe catalyst for the partial oxidation of alkenes to unsaturated aldehydes. When the catalyst is modified by Li, Na, K, and Cs, the acid–base properties of its surface remain unchanged.[37] At the same time, modern physical methods (Mössbauer spectroscopy, EPR, ESCA) have shown that the alkali metals influence the structure of the catalyst. The modified Co–Mo–Bi–Fe catalyst contains the phase $Fe_2(MoO_4)_3$ with a garnet-like structure, which includes an unoccupied dodecahedral sub-lattice. On the introduction of the alkali metals, in particular potassium, whose ionic radius is the optimum for this structure, partial filling of the unoccupied sub-lattice takes place; defects are produced in $Fe_2(MoO_4)_3$, which acquires the structure of a non-stoichiometric garnet containing oxygen vacancies:

$$\square_3^0 Fe_2^{3+}(Mo^{6+}O_4^{2-})_3 \xrightarrow{K^+} K_x^+ \square_x^- \square_{3-x}^0 Fe_2^{3+}(Mo^{6+}O_4^{2-})_3,$$

where $\square^0$ represents a vacancy in the dodecahedral sub-lattice, and $\square^-$ represents an oxygen anion vacancy.

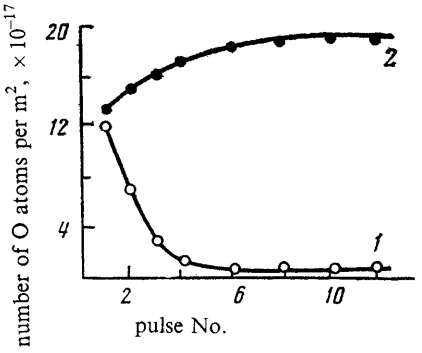


Figure 6. Dependence of the quantity of oxygen of the lattice of the catalysts Co–Mo–Bi–Fe (*1*) and Co–Mo–Bi–Fe–K (*2*) reacting with iso-C_4H_8 in each separate pulse on the number of successive pulses.[38]

These structural changes also have a marked influence on the mobility of the oxygen of the catalyst lattice. Modification of the Co–Mo–Bi–Fe catalyst by potassium leads to an increase in the conversion and the selectivity of the oxidation of isobutylene to methylacrolein. To establish the influence of modification on the

mobility of oxygen of the catalyst, its reduction by isobutylene was studied by the kinetic method and by Mössbauer spectroscopy.[38] Fig. 6 shows the change in the quantity of oxygen reacting in each pulse with isobutylene (size of the pulse 2 ml) in a catalyst with and without the addition of potassium. The concentration of isobutylene on the modified catalyst in each subsequent pulse does not decrease, but increases, and becomes constant after 8–10 pulses. The decrease in the conversion becomes significant only after 25–30 pulses.

The rate of reduction of the catalyst also increases after its modification by potassium. This can be seen particularly clearly after the supply of the fourth or fifth pulse of iso-C_4H_8; at this moment the rate of reduction of the Co–Mo–Bi–Fe catalyst decreases to almost one tenth of the initial rate, and the rate of reduction of Co–Mo–Bi–Fe–K even increases slightly (Table 6). The extent of the reduction of the modified catalyst, that is the quantity of oxygen removed in the reaction with a given number of alkene pulses, is almost ten times greater than that on the catalyst without K.

Table 6. Rate (v_r) and extent (n_0) of the reduction of catalysts by isobutylene.[38]

Catalyst	Conversion of iso-C_4H_8, %	Selectivity of C_4H_6O formation, %	n_0 (atom m^{-2}) after 10 pulses	v_r, μmol m^{-2} s^{-1}	
				initial	after 5 pulses
Co–Mo–Bi–Fe	57	40	$27 \cdot 10^{17}$	0.63	0.05
Co–Mo–Bi–Fe–K	76	83	$18 \cdot 10^{18}$	0.70	0.80

Analysis of the Mössbauer spectra and comparison with the kinetic data obtained in a microcatalytic reactor showed that the reduction of the catalyst involves mainly the oxygen of the $Fe_2(MoO_4)_3$ lattice. When the K ion is introduced into the catalytic system, it is the mobility of the oxygen in this lattice that is increased, as indicated by the spectra of the reduced specimens; in the Co–Mo–Bi–Fe specimen, the extent of the reduction, calculated from the ratio of the normalised areas in the spectrum of Fe^{2+} molybdate to the total area of the spectrum of Fe^{2+} and Fe^{3+} molybdates, is 0.12, whereas that in the Co–Mo–Bi–Fe–K specimen is 0.75.

Modification of the Co–Mo–Bi–Fe catalyst by acidic additives (for example P) leads to a marked deterioration in its catalytic properties.[27] The conversion of C_3H_6 decreases from 87% to 14%, and the selectivity of the oxidation to acrolein decreases from 60% to 32%. The introduction of phosphorus, like that of potassium, produces practically no change in the acid–base properties of the catalyst surface. X-Ray diffraction and Mössbauer spectroscopy have shown that the presence of phosphorus prevents the formation of crystalline iron(III)molybdate in the catalyst. The rate and extent of the reduction of the Co–Mo–Bi–Fe–P catalyst by propylene are ten times lower than those for Co–Mo–Bi–Fe.

Thus the change in the catalytic characteristics of oxide systems under the influence of alkaline and acidic additives is not always due to their influence on the acid–base properties of the catalyst surface.[39] As shown above, these additives influence mainly the structure of the solid and the mobility of the reactive oxygen, leading to a change in the selectivity of the oxidation processes.

2. Silver catalyst

Only the metallic catalyst silver is used for the partial oxidation of ethylene to ethylene oxide. This process has been the subject of a large number of studies[5,6,8] to determine the mechanism of formation of C_2H_4O, the nature of the surface of the catalyst, the state of oxygen, etc. Modification by alkaline and acidic additives (K, Cs, Cl, etc.) is widely used to produce an active and selective silver catalyst.

To determine the mechanism of the action of the additives, it is necessary to examine the forms of oxygen adsorbed on silver, taking part in the oxidation of ethylene.

The following scheme has been given[40] for the reaction of oxygen with silver:

1. $O_2 + Ag \rightarrow O^-_{2\,ads} + Ag^+$,
2. $O_2 + 4Ag(\text{individual atoms}) \rightarrow 2O^{2-}_{ads} + 4Ag^+$,
3. $O_2 + 4Ag(\text{aggregate of atoms}) \rightarrow 2O^-_{ads} + 4Ag(\text{aggregate})$.

Other authors[41,42] consider that isolated silver atoms adsorb oxygen in the molecular form, which then takes part in the oxidation of C_2H_4 to C_2H_4O. Carbon dioxide is formed by the reaction between C_2H_4 and atomic oxygen, which is adsorbed on the aggregate (4Ag). A different view is held by other workers,[43] who consider that the formation of C_2H_4O also involves atomic oxygen. In addition to the production of surface forms, the adsorption of oxygen on polycrystalline silver is accompanied by its solution in the layers of the metal lattice next to the surface.[44]

In the opinion of other workers,[45] dissolved oxygen weakens the bonds between the surface forms of oxygen and the catalyst. The study by modern spectroscopic methods of the action of alkali metal ions adsorbed on different faces of silver showed that these additives increase the rate of the recombination of atomic oxygen to molecular oxygen, and hence increase the degree of covering of the surface by molecular oxygen. Thus on the (111) face of silver on which caesium ions were adsorbed, an oxygen-containing surface structure was detected.[46,47] The addition of caesium decreases the rate of the extensive oxidation of ethylene and alters the activation energy of formation of CO.

Modification of silver by caesium ions changes not only the concentration of oxygen on the surface but also the rate of isomerisation of C_2H_4O.[48]

When the Rb^+ ion is added to silver, the formation of peroxide leads to the production of molecular oxygen by the reaction

$$2\,Rb_2O_4 \rightarrow 2\,Rb_2O + 3\,O_2,$$
$$2\,Rb_2O \rightarrow 4\,Rb + O_2$$

The introduction of the K^+ ion into Ag (110 face) also alters the degree of covering of the surface by oxygen; K_2O_4 is formed, and decomposes by a scheme similar to that for rubidium peroxide.[50]

The addition of alkali ions to silver alters the ratio of the rates of formation of C_2H_4O and CO_2 in the oxidation of ethylene, and also the activation energies of these reactions, so that it influences the selectivity of the process.

The introduction of the Cl ion into a single crystal of Ag (111 face) leads to the displacement of the previously adsorbed oxygen atom.[51] Changes are observed in the rate and order of the

reaction and in the activation energy for the formation of ethylene oxide and CO_2, depending on the degree of covering of the surface by chlorine (Fig. 7). According to other data,[52] chloride ions adsorbed on silver form a surface structure of silver chloride AgCl. The adsorption of Cl ions increases the diffusion of oxygen atoms into the silver lattice.[53]

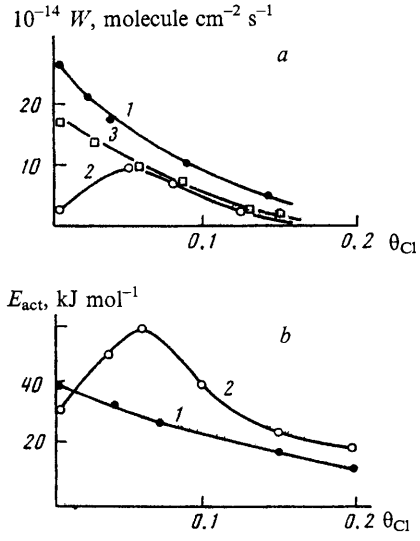


Figure 7. Effect of the degree of covering of the silver surface with chlorine on the rate (*a*) and activation energy (*b*) of formation of ethylene oxide and CO_2:[51] *1*, carbon dioxide; *2*, ethylene oxide; *3*, total rate of transformation of ethylene.

Silver is often modified by chlorine by introducing dichloroethane into the reaction mixture. This method of introducing additives has been called "gas modification",[2] and its mechanism is the same as the usual mechanism of action of additives introduced into a catalyst. On the silver surface, dichloroethane dissociates to form AgCl.[5] Experiments using the ^{36}Cl isotope have shown that the silver chloride formed in the reaction medium is reduced with the generation of a Cl ion, which does not migrate into the metal lattice at 330 °C, but remains on the surface. Similar results were obtained using the ^{131}I isotope.

In the modification of silver, dichloroethane undergoes the following transformations:

$$C_2H_4Cl_2 + Ag \rightarrow Ag(C_2H_4Cl_2)_{ads} \xrightarrow{O_2} \overbrace{Ag[AgCl] + (Cl^-)_{ads}}^{} + C_2H_4.$$

Dichloroethane added to the $C_2H_4 + O_2$ reaction mixture inhibits the dissociation of oxygen on silver.[54] The concentration of the modifying additive appears in the kinetic equation for the reaction.

Thus when the potassium ion is introduced into the silver catalyst:

1, the chemisorption of oxygen is increased,

2, peroxides generating molecular oxygen are formed,

3, the rate of recombination of oxygen atoms increases,

4, the rate of isomerisation of ethylene oxide changes,

5, the kinetic parameters of the oxidation of ethylene change.

When the chloride ion is added:

1, the rate of dissociation of molecular oxygen decreases,

2, the strength of the Ag–O bond decreases,

3, the rates of desorption and recombination of oxygen atoms and their diffusion into the Ag lattice increase,

4, chloride ions displace oxygen atoms from the silver surface,

5, the kinetic parameters of the oxidation of ethylene are altered.

Modification of silver influences not only the state of the adsorbed oxygen but also the adsorption of C_2H_4. Ethylene is adsorbed on the silver surface only in the presence of oxygen, reacting with it to form surface complexes whose structure has been studied by infrared spectroscopy.[55] It was previously shown that on adsorption, ethylene is positively charged, but the work function depends on the magnitude of the negative charge on oxygen. The presence of the Ag surface of additives with positive (alkali metals) or negative (halogens) charges alters the heats of adsorption and the bond energies of oxygen and ethylene–oxygen complexes with the surface. This electronic factor should probably also influence the activation energies of the partial and extensive oxidation of ethylene. A study of the combined adsorption of potassium and chlorine on the (100) face of a single crystal of Ag showed that an electrostatic interaction takes place between the Cl^- and K^+ ions.[56] AgCl, stabilised by K^+ ions, is formed on the surface. In addition, KCl, desorbed at 700 K, was also detected.

Thus as in oxide systems, the introduction of acidic and alkaline additives into silver influences chiefly not the acid–base properties of the surface but the forms in which oxygen is adsorbed on the metal, and also the kinetics of the oxidation of ethylene to ethylene oxide.

V. Summary

The term modification is now used to describe not only the introduction of additives into different catalysts but also the change in the quality of the surface, for example the replacement of OH groups in silica gel by various elements, the deposition of various complexes and molecules on the surface, etc.

It is assumed[57] that the modification of simple and complex catalytic systems involves a change in the structure of the solid or a reconstruction of its surface, and also a change in the energy of the bonds between the adsorbed reagents and the surface. It has been noted that modified systems are multi-functional, and that the selectivity can be controlled by controlling their structure.

Attention was drawn above to the fact that practically all selective oxidation catalysts are multi-phase (even in the case of solid solutions, for example $Sb_2O_4-SnO_2$).

Modern spectroscopic methods have detected the migration of the additive from the bulk to the surface with the formation of a separate phase in both oxide and metallic catalysts. When silver is modified by alkali and halide additives, new compounds, peroxides and salts, are produced on the surface.

Since modified catalysts are multi-phase, a separation of functions between different phases has been suggested.[58,59] An example is provided by the oxidation of propylene on a cobalt–molybdenum oxide catalyst modified by Bi and Fe, which consists of Co, Bi, and Fe molybdates. During the oxidation of propylene under stationary conditions, partial reduction of the molybdate $Fe_2(MoO_4)_3$ to $FeMoO_4$ takes place, with the production at the interface between these phases of a super-equilibrium concentration of vacanices, which, by diffusing to the $Fe_2(MoO_4)_3/\beta$-$FeMoO_4$ interface, can act as centres for the dissociative adsorption of oxygen from the gas

phase with the formation of lattice oxygen. The transfer of this oxygen to the active regions of the surface, on which the alkene is adsorbed and oxidised, takes place via the interface between the iron and bismuth molybdate phases. A possible model of a system of this kind is shown in Fig. 8. The phase transitions $Fe_2(MoO_4)_3 \rightleftarrows FeMoO_4$ are facilitated if the catalytic system contains the isostructural phase β-$CoMoO_4$, since the interphase boundaries of β-$FeMoO_4$ and β-$CoMoO_4$ are coherent, and the formation of $FeMoO_4$ in the presence of a sufficient quantity of anion vacancies is associated with practically no energy barrier.

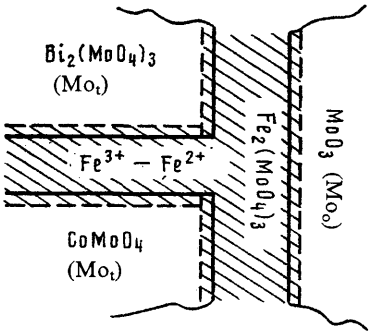


Figure 8. Model of the boundary zone of a Co–Mo–Bi–Fe–O catalyst;[60] Mo_o and Mo_t correspond to octahedral and tetrahedral coordination of the molybdenum ion.

The quantity of anion and cation defects depends on the total extent of the interface between the crystallites of the different phases in the catalyst, and this extent in turn is determined by the size of the actual crystallites, that is by their degree of dispersion. The degree of dispersion of multi-phase and multi-component oxide catalysts based on the molybdates of various divalent metals depends on their composition.[60]

A study of the oxidation of propylene to acrolein on complex oxide catalysts with the general formula $M^{II}_6Mo_{12}Bi_{0.5}Fe_{0.75}O_x$, where M^{II} = Co, Mg, Zn, Mn, established that the highest catalytic activity is shown by the systems with M^{II} = Co and Mg.[60] The Co and Mg molybdates in these systems, like the other phases, are characterised by the maximum degree of dispersion. For M^{II} = Zn and Mn, the individual crystallites are much larger, and the activity of these catalysts is much lower. At the same time, it was shown that the chemical nature of the cation M^{II} in this complex catalyst has practically no influence on the overall activity; in this case the catalytic properties are influenced significantly by the degree of dispersion. The additives introduced into complex oxide catalysts can be divided into two types: those of one type take direct part in the functioning of the active centre and facilitate some stage of the process (for example Fe ions in the Co–Mo–Bi–Fe catalyst), while those of the other type create a definite "macro-structure" (for example Co and Mg ions in the M^{II}–Mo–Bi–Fe system). The action of additives of the first type is called "micro-modification", and that of the second type "macro-modification".[60]

The effect of modification is revealed particularly clearly in the action of the alkali metals on a catalyst. These additives are capable of producing new basic centres on the surface. In addition, the alkali metals can form new compounds (for example salts, bronzes in the case of vanadium catalysts, etc.) and hence increase the multi-phase character of the catalytic system. The alkali metals may also be introduced into the structure, facilitating its rearrangement (for example, when the K^+ ion is introduced into iron molybdate with the garnet structure, it acquires a non-stoichiometric structure with a larger number of defects). All these changes influence the state of oxygen in the catalytic systems. It is believed[61] that the modification by alkali metals of oxide catalysts for the oxidation of hydrocarbons alters the ratio of nucleophilic and electrophilic oxygen on the surface. It is suggested that these forms are involved in the oxidation. To achieve a high selectivity of partial oxidation, it is necessary to suppress extensive oxidation. Both processes involve molecular and atomic oxygen and the oxygen of the oxide lattice. Additives control the concentrations of these forms of oxygen on the oxide surface, and hence alter the ratio of the products of mild and extensive oxidation.

In the present review, most attention has been paid to the promoting action of additives and its mechanism. Increase in the concentration of additives in a catalyst beyond a certain limit, however, decreases the reaction rate and alters the activation energy. The mechanism of this "poisoning" is less clear, and has been little studied. Increase in the concentration of additive probably leads to an increase in the concentration in the system of new compounds which in a number of cases are inactive and decrease the number of active centres. For example, with increase in the concentration of iron ions in the Co–Mo–Bi–Fe system, the products include not only iron molybdate but also iron oxide, on which propylene undergoes extensive oxidation, so that the selectivity of the formation of acrolein from the alkene decreases sharply. This phenomenon is particularly characteristic of solid solutions, in which increase in the quantity of additive exceeds the solubility limit, and an inactive oxide phase separates. In addition, the active centres of the catalyst may be blocked by additive ions, as observed on a silver catalyst with increase in the concentration of Cl^- ions.

The decrease in activity with increase in the concentration of an additive may also be due to a phase transition in one of the compounds in the catalyst. For example, increase in the vanadium concentration in the V_2O_5–TiO_2 system leads to a phase transition in TiO_2 from the rutile to the anatase structure,[62] and the catalyst is deactivated.

The decrease in the catalytic activity of modified catalysts may also be due to reaction between the reaction medium and the solid. The optimum concentration of additives ensuring the maximum activity of a catalyst can be lost by the partial removal of the elements of these additives by the reaction mixture. This takes place, for example, with the phosphorus ion in a V–Ti–P oxide catalyst[62] or with the Cl ion in a silver catalyst.[5] Decrease in the concentration of the additive lowers the activity of the catalyst, and mimics its "poisoning".

In catalytic oxidation, electronic interaction takes place between the ions in the catalyst. At the optimum concentration of the additive, these transitions are facilitated, since a new lattice structure facilitating the transport of electrons is produced. If the concentration of additive exceeds the optimum value, breakdown of the relative arrangement of these ions and the production of electron traps become possible. In this case there is also a decrease in the rate of individual reactions, and "poisoning" of the catalyst takes place.

Thus the modification of various catalytic systems involves the formation of new compounds in the bulk and on the surface of the catalysts, and changes the number and composition of the active

centres, the structure of the solid, its ability to undergo rearrangement, and the electronic interactions between the elements in the catalyst. Additives influence the kinetics (reaction rate, activation energy) and mechanism (structure of surface compounds, energies of their bonds with the surface) of a reaction.

It is difficult to predict the action of different additives, since they influence many functions of catalysts. Modification, however, makes it possible to produce effective catalysts for the oxidation of various organic compounds.

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