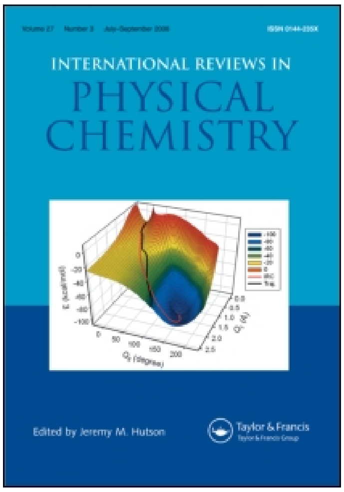

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Modification of catalysts

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Modification of catalysts

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The effect of additives on metal oxide and silver catalysts to improve the activity and selectivity of various processes is considered. Additives influence the kinetic parameters of a process (rate and activation energy) and the reaction mechanism (structure of surface compounds, energy of their bond with the catalyst). Modification causes the formation of new compounds in the bulk and at the surface of the catalyst, thereby altering the composition of active sites and inducing formation of other sites. The effects of species added to multicomponent oxide systems, as well as various aspects of modification by acid–base additives are considered. Specific features of the influence of additives and the role of modified multifunctional catalytic systems are also discussed.

1. Introduction

In general, the positive (promoting) and negative (poisoning) effects of additives are readily distinguished, and they are accordingly classfied as promoters and poisons (Maxted and Evans 1937). Poisoning was thought simply to block the active surface of the catalyst, but the much more complicated promotion mechanism remained uncertain.

A new phenomenon called ‘modification’ was discovered in the 1940s. It consists of dual and specific changes in the catalyst activity in the presence of certain additives. These changes cannot be unconditionally called either poisoning or promotion because the same additives behave at times as promoters and sometimes as poisons (Roginskii 1947, Margolis and Todes 1950, Margolis and Krylov 1950). An example is given by the variations of the rate constant (figure 1), the activation energy and the pre-exponential factor (figure 2) in total iso-octane oxidation with certain changes in the concentration of NaOH introduced into WO_3. Extremal dependences of the reaction kinetics on the concentration of the additives has been observed not only for WO_3, but also for more complex catalysts (spinels, and others). Characteristic curves for the dependence of the logarithm of the rate constant on inverse temperature are observed for catalysts with different concentration of additives (figure 3). A catalyst with a certain concentration of the additive may manifest the highest activity in one temperature region and be less active in another. This is due to concerted changes in the activation energy and the pre-exponential factor as a function of the additive amount. At the same constant amount of the latter, the catalyst activity can increase over a certain temperature range but at other temperatures it may decay. At the same temperature the additive in a certain concentration will raise the catalyst activity, but lower it when taken in a higher amount. For modification the dependence of activity on the additive concentration becomes extremal. As mentioned earlier improvement in catalyst activation is called promotion, its deterioration poisoning. The experimental results obtained in the U.S.S.R. on the modifying effect of some additives were given in a review by Tolpin *et al.* (1953). However, the regularities observed on introduction of additives into catalysts for the total oxidation of olefins were found to be the same as for catalysts

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of partial oxidation, such as that of C_2H_4 to C_2H_4O over Ag, and C_3H_6 to C_3H_4O over CuO–Cu_2O and NiO (Margolis 1977). It was found, for instance, that partial hydrocarbon oxidation also displays extremal dependences on the reaction rate and activation energy on the additive concentration (Grant and Harback 1987).

Virtually no catalysts containing an individual oxide or metal are used at present. Table 1 lists certain modified catalysts for various reactions (Alkhazov and Margolis 1988). The modification mechanism is still ill defined. The available experimental results have not been generalized. Only a few reviews have focused on this topic. One was published by Thompson (1987), who, *inter alia*, described results obtained in the promotion of various metals and oxide catalysts for Fischer–Tropsch synthesis and CO hydrogenation. It also deals with the promoting effect of the support, the catalyst lifetime prolongation due to additives and its possible effect on the reaction mechanism.

One proposal to explain the mechanism of modification is in terms of the zone theory of semiconductors, namely by changes in the Fermi level of crystals (Vol'kenshtein 1978). The suggestion is that the additives may alter the electronic properties of the crystal both in the bulk and at the surface. Consequently the catalytic activity of samples must be correlated with the electronic characteristics of a solid, such as conductivity or the electron work function. The electronic donors or acceptors are thought to change both the Fermi level position and the catalyst surface coverage by reactants that are charged on adsorption becoming acceptors or donors of electrons.

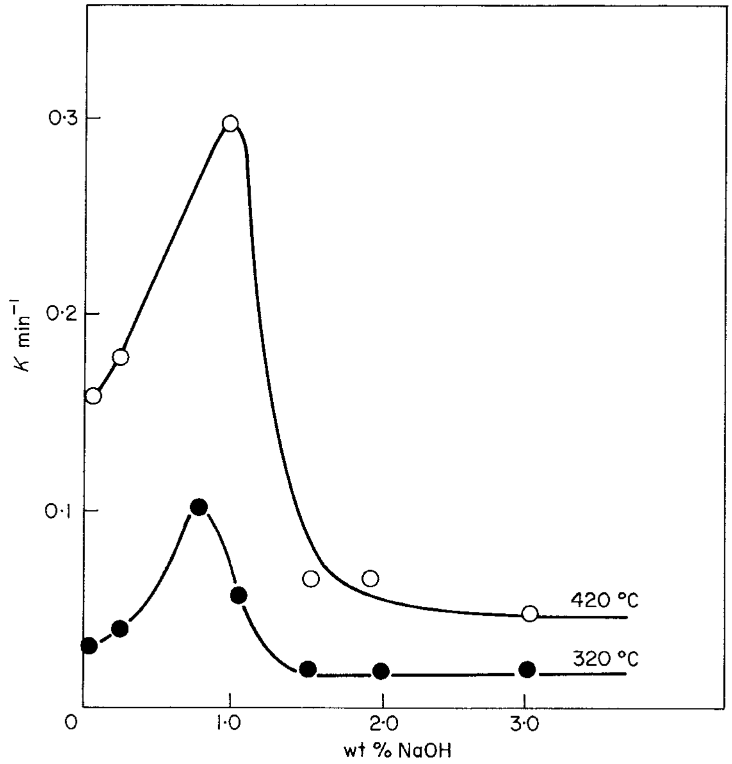

Figure 1. Effect of the NaOH additive on the rate constant of iso-octane oxidation over tungsten oxide (Margolis and Krylov 1950).

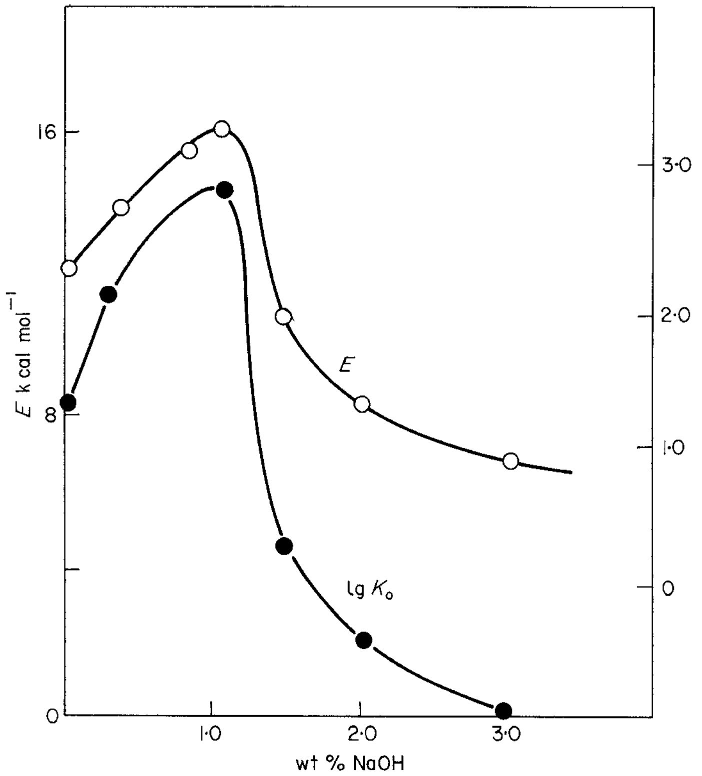

Figure 2. Effect of the NaOH additive on the activation energy and the pre-exponential logarithm in total iso-octane oxidation over tungsten oxide (Margolis and Krylov 1950).

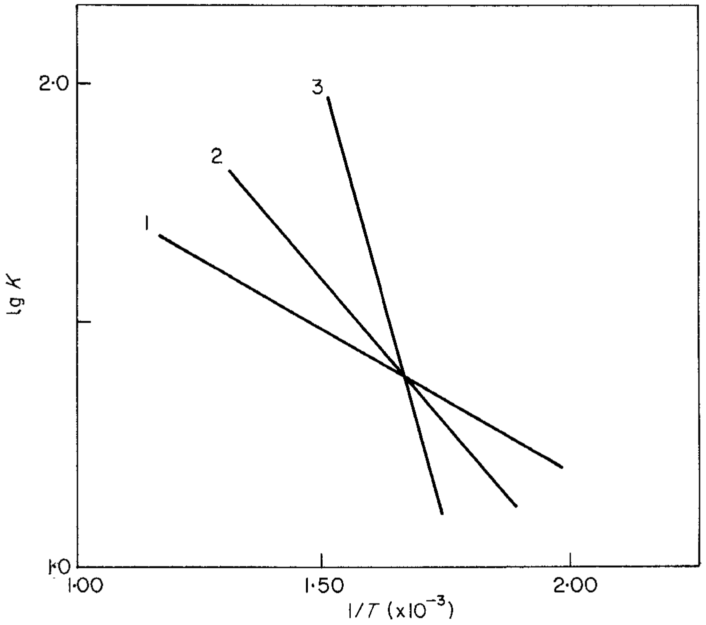

Figure 3. Schematic dependence of log k on $f(1/T)$ for various additive concentrations (Margolis and Todes 1950).

Table 1. Modified catalysts (Alkhazov and Margolis 1988).

Reaction	Catalyst composition components	
	Basic	Additives
Oxidation		
$C_2H_4 \rightarrow C_2H_4O$	Ag	Cl, K, Rb, Cs
$C_3H_6 \rightarrow C_3H_4O$ $i\text{-}C_4H_8 \rightarrow C_4H_6O$	Co–Mo–O	Bi, Fe, K, Sb
$C_3H_6 \rightarrow C_3H_6O$	Sn–Mo–O	Fe, K
o-xylene→phthalic anhydride	V–Ti–O	K, Cs, Rb, P
Butane→maleic anhydride	V–P–O	Zn, Sb, Ni

This can even induce a change in both the rate-limiting step of a process and its rate (see also Margolis (1977)). However, the same additive can be differently charged in the bulk and at the surface of an oxide. Depending upon the distribution of the additives in a solid, their electronic characteristics can differ and their effect on the process rate can be inadequate.

For metals the additives and the reactants have been thought to form charged surface dipoles. Their electrostatic interaction could result in different surface coverage by the reactants, thus influencing the reaction rate. However, it was found that the modification of Ag by donors or acceptors could not be ascribed merely to dipole interaction (Margolis 1977). The electron work function variations caused by modification of Ag cannot be the reason for changes in the catalyst activity or process selectivity. It points only to changes in the solid surface properties in the presence of additives.

The wide scope of the results obtained for various catalytic systems (metals, simple and complex oxides) cannot be explained solely by the changes in electronic properties of the solid. The modification of catalysts seems to be a complex phenomenon and the effects of additives on the solid structure, the valences of the catalyst components, the adsorption of reactants, the reaction kinetics, and so on, should be considered to elucidate this phenomenon.

Certain simple and complex oxide catalysts and a metal catalyst, silver, were chosen out of the many modified catalytic systems in discussing the effects of additives.

2. Modification of metal oxides

Additives in metal oxide systems can occupy lattice vacancies; they can also form solid solutions (substitution or incorporation) and other chemical compounds, thus changing the energy spectrum of a catalyst, and the electronic properties of its bulk and surface. Usually additives are introduced into oxide catalysts in considerable amounts and consequently such catalysts are classified as strongly alloyed (Bonch-Bruevich 1965). The distribution of additives in the bulk and at the surface of catalysts, their effect on the Fermi level position and their adsorption characteristics have been discussed in terms of the zone model of semiconductor crystals. The interactions between defects and additives can also cause structural changes in a catalyst. The defects (lattice vacancies) or the incorporated additives can become completely ordered to form a superstructure. In oxide systems the ordering of defects occurs by rearrangement of bonds between coordinated polyhedrons, the Mo : O ratio changes on certain crystal faces. In the catalyst reduction by a hydrocarbon, the oxygen ions 'evaporate' from the upper plane of the crystal surface with subsequent migration of adjacent cations and anions to the octahedral vacancies appearing in the structure. Persistent reduction results in repeated occurrence of the process and in a greater crystallographic shift (Tret'yakov 1979).

In the oxidation of propylene to acrolein on copper oxide, the additives induce changes that are characterized by the modification in the rates and activation energies of the products generation. For instance, the addition of lithium ions to CuO increases the energy of acrolein formation from 12 to 22 kcal mol^{-1}, and lowers that of CO_2 from 26 to 16 kcal mol^{-1}. There also occurs a significant change in the pre-exponential factors. In the series of lithium-modified phosphate ions and copper oxide–antimony ions, the pre-exponential factor regularly increases from 10^{17} to 10^{22} in the order $CuO+Li<CuO+PO_4^{3-}<CuO<CuO+Sb^{3+}$. The higher pre-exponential factor can be due to a change in the number of catalyst active sites, caused by introduction of the additives.

Vanadium pentoxide modified by various additives is widely used for partial oxidation of aromatic hydrocarbons. For instance the Sn, Ti, Mo additives improve the selectivity of benzene oxidation to maleic anhydride, and of naphthalene and *o*-xylene to phthalic anhydride (Yoshida *et al.* 1973). The presence of Sn^{4+} in V_2O_5 increases the rate of the catalyst reduction (i.e. favours the oxygen migration in the lattice). Yoshida *et al.* (1973) came to the conclusion that Ti^{4+} stabilizes the V_2O_5 structure, and the Sn^{4+} ions enhance the increase in lattice defects. The concentration of V^{4+} ions in a catalyst increases in the presence of TiO_2 (i.e. the incorporation of SnO_2 weakens the $V=O$ bond). The extent of naphthalene conversion into phthalic anhydride grows over V_2O_5 modified by Sn^{4+} ions, compared with non-modified V_2O_5. This is evidence of an essential effect of the $V=O$ bond energy on naphthalene oxidation.

The pentoxide structure specificities contribute to its ready interaction with foreign metal ions to form vanadium bronzes—double non-stoichiometric oxides of a general formula A_xBO_3 that possess a characteristic semiconductor or metal conductivity (Fotiev *et al.* 1978). The formation of bronzes can be interpreted as the result of incorporation of foreign atoms or ions into the matrix. Metal A that penetrates into the lattice and occupies a part of the free nodes has no effect on the structure of the basic lattice. The presence of A results in appearance of an impurity level in the forbidden BO_3 zone below the conductivity zone, or in the zone as such that appears to be 'populated' by the metal A electrons. With alkali metals and silver the formation of bronzes is particularly ready. Besides, for oxidation of aromatic hydrocarbons and aldehydes use is made of the V–Mo oxide systems representing a solid solution of MoO_3 in V_2O_5 (V: Mo = 1 : 0·27) with silver and copper additives. The X-ray, IR spectroscopy and EPR results showed the formation of bronzes with differently located vanadium ions. Such structures change the oxidation rates of hydrocarbons. The coefficient of oxygen diffusion in V_2O_5 was found to be 10^{-8} cm^2 s^{-1}, and for bronzes it was by two orders higher (Volkov and Novak 1980), which is due to the cavities in bronze structures that permit ready migration of oxygen (Yoshida *et al.* 1973).

Great attention is paid to the V–Mo oxide system widely used in the oxidation of aromatic compounds. V_2O_5 is introduced into MoO_3 in different concentrations drastically changing the activity and the process selectivity as a function of the vanadium content in the sample. The VMo_3O_{11} compound is an active component of the V–Mo oxide catalyst for acrolein oxidation to acrylic acid. Its maximal amount in the system was observed for 7–15 mol % V_2O_4. Other compounds—VMo_2O_{8+x} and

$V_6Mo_4O_{25}$—were also formed (Andrushkevich and Kuznetsova 1986). CuO is an effective additive to the V–Mo catalyst in the production of acrylic acid (Kuznetsova 1984). The Cu ion causes the appearance of a transient composition compound, which according to X-ray, XPS and IR spectroscopy is formed from VMo_3O_{11} and VMo_2O_{3+x}.

An active catalyst for benzene oxidation to maleic anhydride is obtained by introduction of MoO_3 into V_2O_5. Besides the formed $V_9Mo_8O_{40}$ compound V^{4+} ions also appear. From the EPR results their maximal concentration corresponds to the solubility limit of MoO_3 in V_2O_5 (about 30 mol %) (Bielanski *et al.* 1971). The rate of benzene oxidation to maleic anhydride, as well as the process selectivity depend on the concentration of V^{4+} ions in the catalyst. The catalytic activity change in benzene oxidation occurs here in the same way as that for the V^{4+} concentration.

In specifying the redox mechanism of partial organic oxidation on the V–Mo oxide system (V : Mo = 1 : 3) the EPR method was used *in situ* in order to follow the V^{4+} generation in the oxidation of allyl alcohol to acrolein (Makarova 1987). The reduction and oxidation of the catalyst occurs as

$$V^{5+}O^- + C_3H_5OH \rightarrow V^{4+}\square^\circ + C_3H_4O + H_2O$$

$$2V^{4+}\square^\circ + O_2 \rightarrow 2V^{5+}O^-$$

where $\square$ stands for the anionic oxygen vacancy. The rate of allyl alcohol oxidation is found to be proportional to the amount of V^{4+} ions in the catalyst.

A V–Ti oxide catalyst is used for *o*-xylene oxidation to phthalic anhydride. When V_2O_5 is introduced into titanium dioxide, the maximal rate of phthalic anhydride generation and the process selectivity are observed for a 2·5–8 mol % V_2O_5 content in the system. Vanadium ions coordinately bound with titanium ions and a V_6O_{13} compound are generated in this system (Wachs *et al.* 1985). As shown by the EXAFS method (Kozlowski *et al.* 1983), titanium dioxide contributes to the disordering of V_2O_5 in the V–Ti catalyst.

In order to obtain acetone on propylene, a Sn–Mo system was obtained by modification of inactive SnO_2 by molybdenum ions (Sn : Mo = 9 : 1). From the X-ray, IR and UV spectroscopy results (Alkhazov *et al.* 1982), this system consists of a solid solution of MoO_3 in SnO_2, and of MoO_3, and SnO_2 oxides.

Thus, as shown by certain examples, the modification of simple oxides by various additives provides new catalytic systems consisting of solid solutions, other compounds, and microheterogeneous systems with catalytic properties differing from those of the initial simple oxides.

3. Effects of additives on complex oxide systems

Bismuth and cobalt molybdates are two systems most widely used for oxidation of propylene to acrolein, and the tin–molybdenum oxide catalysts for oxidation to acetone. The vanadium molybdenum system also converts aromatic hydrocarbons into anhydride and vanadium phosphate catalysts are used for oxidation of butane to maleic anhydride. The additives improve the effectiveness of these systems.

The incorporation of Fe into bismuth molybdate results in a complex oxide system involving a ternary Bi–Mo–Fe compound and Bi and Fe molybdates. Table 2 lists the results obtained for the effect of the catalyst modification by Fe on the rate and selectivity of C_3H_4O generation from C_3H_6 (Notermann *et al.* 1976). The ternary

Table 2. Influence of the Fe ion on the Bi–Mo catalyst activity and selectivity (Notermann *et al.* 1976).

Fe^{3+} concentration (at %)	Phase composition	Acrolein formation rate at 340°C ($ml\,m^{-2}\,min^{-1}$)	Selectivity in acrolein (%)
—	$Bi_2(MoO_4)_3$	0·44	88
2	$Bi_2(MoO_4)_3$ $Fe_2(MoO_4)_2$ Tertiary compound	1·32	98
14·8	$Bi_2(MoO_4)_3$ $Fe_2(MoO_4)_3$ Tertiary compound	3·75	91
33·3	Tertiary compound Bi : Fe : Mo 1 : 1 : 1	0·58	87

Table 3. Modification of $CoMoO_4$ (Linde *et al.* 1983).

Catalyst composition	Phase composition
Co–Mo	α-$CoMoO_4$; β-$CoMoO_4$; MoO_3
Co–Mo–Bi	α-$CoMoO_4$; β-$CoMoO_4$; MoO_3; $Bi_2(MoO_4)_3$
Co–Mo–Bi–Fe	α-$CoMoO_4$; β-$CoMoO_4$; $Fe_2(MoO_4)_3$; $Bi_2(MoO_4)_3$
Co–Mo–Bi–Fe–Sb	α-$CoMoO_4$; β-$CoMoO_4$; $Fe_2(MoO_4)_3$; $CoSb_2O_6$; $Bi_2(MoO_4)_3$

Bi–Mo–Fe compound taken apart is low-active and comparable in catalytic activity to bismuth molybdate. Modification of $CoMoO_4$ by Bi, Fe, Sb induces a drastic change in its calalytic activity.

X-ray analysis shows that new compounds are also formed in these systems (Table 3).

The Co–Mo–Bi–Fe–Sb–O catalytic system is used for partial oxidation of isobutene to methyl acrolein. The structural changes in this multicomponent oxide system caused by varying the amounts of Bi and Fe additions have been studied by X-ray diffraction and Mössbauer spectroscopy (Maksimov *et al.* 1983). Besides the basic matrix structure of $CoMoO_4$ the catalyst was found to contain $Bi_2(MoO_4)_3$ and $Fe_2(MoO_4)_3$, as well as a complex compound of the $M_3FeMo_2O_{12}$ type (M = Bi, Sb). Figures 4 and 5 present the results on i-C_4H_8 conversion and the relative content of the $Fe_2(MoO_4)_3$ and $M_3FeMo_2O_{12}$ phases as a function of the Bi and Fe concentrations in $Co_6Mo_{12}Bi_xFe_ySb_1O_x$. The maximal i-$C_4H_8$ conversion was observed for concentrations of Bi ($x=1$) and of Fe ($y=4$–6), both Fe-containing phases being present in the same amount.

Many results obtained in recent years show that the interaction of biographic defects in oxide crystals containing additives can cause structural changes in the catalyst bulk. The defects can become ordered, and the ratio of metal ions to oxygen in various crystal planes can change. Some defects can interact with the main oxide lattice component to form intermediate phases. A disordering of defects can result in atom assemblies with appearance of clusters.

As found by Sleight and Linn (1976), a complex molybdenum catalyst of a scheelite structure containing Mo, Bi and Pb ions can have a different number of defects formed

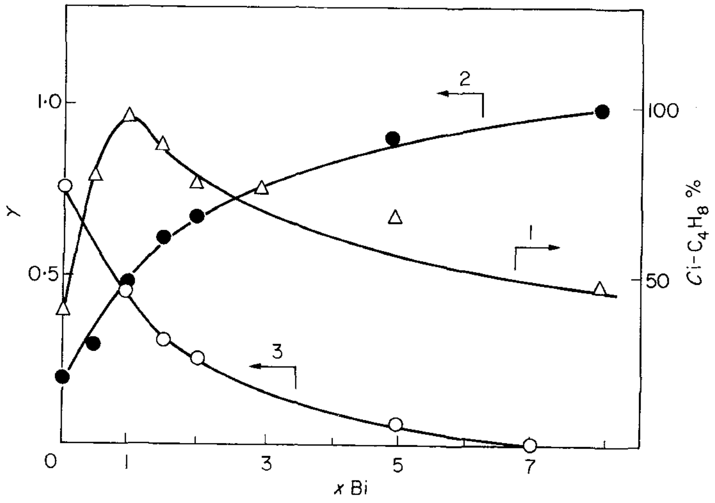

Figure 4. Change in isobutylene conversion at 370°C (1) and in the relative content of phases $BiFeMo_2O_{12}$ (2) and $Fe_2(MoO_4)_3$ (3) as a function of the bismuth amount in the catalyst (Makisimov *et al.* 1983).

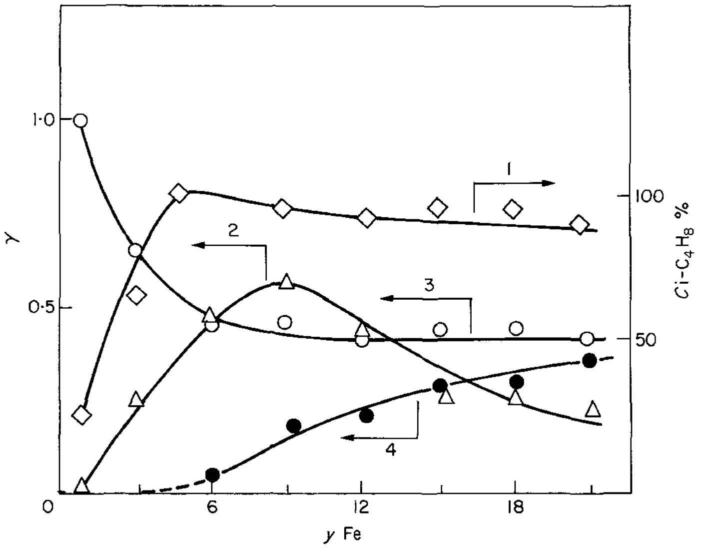

Figure 5. Change in isobutylene conversion at 370°C (1) and in the relative content of phases $Fe_2(MoO_4)_3$ (2), $Bi_3FeMo_2O_{12}$ (3) and α-Fe_2O_3 (4) as a function of the iron content in the catalyst (Maksimov *et al.* 1983).

in the presence of Pb ions (lattice vacancies). With increasing concentration of structural defects, the extent of C_3H_6 conversion into C_3H_4O over this catalyst becomes higher.

Besides the cationic defects, there can appear anionic defects caused by oxygen migration. Thomas *et al.* (Thomas 1988, Buttrey *et al.* 1986) have shown that the many phases of bismuth molybdates capable of catalysing the selective oxidation of propylene are derived from defect fluorite.

It has been repeatedly reported (Margolis 1977, Keulks *et al.* 1979, Maksimov *et al.* 1983, Thomas 1988) that, as found by the isotope and redox methods, selective organic oxidations over oxide systems involves the catalyst lattice oxygen.

The formation of various non-stoichiometric oxides exemplified by MoO_3 reduction with one of the components undergoing oxidation is discussed in a monograph by Krylov and Kiselev (1981). No essential rearrangement of the lattice with phase conversions is observed. There occurs only a 'crystallographic shift': reduction causes a partial escape of oxygen from the lattice, vacancies are formed, the distance between Mo ions becomes shorter, and the bonding of oxygen octahedrons around Mo ions suffers a change. There appear blocks of a relatively stable structure constructed of blocks of smaller dimensions and separated by shift planes of another regular structure.

The MoO_3 reduction leads to formation of a Mo^{5+} ion, as a result of fast migration of an electron into the bulk, and its capture by Mo^{6+} in the vicinity of the vacancy

$$Mo_s^{6+}O_s + RH \rightarrow \left[Mo_s^{5+} \ldots \overset{H}{O}_s \right] R^+ \xrightarrow{+Mo_v^{6+}O_v} Mo^{6+}\square RO + Mo_v^{5+}O_v + H^+$$

The vacancy is drawn from the surface to the defect. As equivalent to the vacancy migration, oxygen diffuses to the surface by the multishift mechanism of microblocks. In this way the catalyst surface layer is constantly rearranged in the course of the reaction and the oxygen atoms exchange places.

The introduction of additives into such systems acts on the rates of oxygen migration and rearrangement in the oxide lattice which govern the oxygen mobility in the lattice. Ueda *et al.* (1986) have found using ^{18}O that oxygen migration in a $Bi_{1-x/3}V_{1-x}Mo_xO_4$ system in the course of C_3H_6 oxidation to C_3H_4O depended on the catalyst composition. Table 4 lists the rates of reduction by hydrogen and the mobilities of lattice oxygen in catalysts of different composition.

It will be noted that the variations in the rate of reduction of the above systems with H_2 are opposite to those for reduction with C_3H_6, the nature of the reducing agent (H_2 or C_3H_6) plays an essential role. The reduction rate dependence on the reactant nature seems to be connected with the difference between the active sites where the interaction with the catalyst oxygen occurs. The increase of the concentration of additives in the catalyst changes its surface composition and the number of active sites thus influencing the reaction rate and the catalyst activity.

Quantitative results on the reduction by C_3H_6 of $CoMoO_4$ modified by Fe and Bi have been obtained by a microcatalytic method combined with Mössbauer

Table 4. Characteristics of $Bi_{1-x/3}V_{1-x}Mo_xO_4$ catalysts (Ueda *et al.* 1986).

X	Surface concentration of Bi (at %)	Rate of reduction in H_2 (10^{-6} mol min^{-1} m^2)	Mobility of lattice oxygen ions (%)†
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

† Fraction of the lattice oxygen ions involved in oxidation in respect to the total amount of lattice oxygen ions.

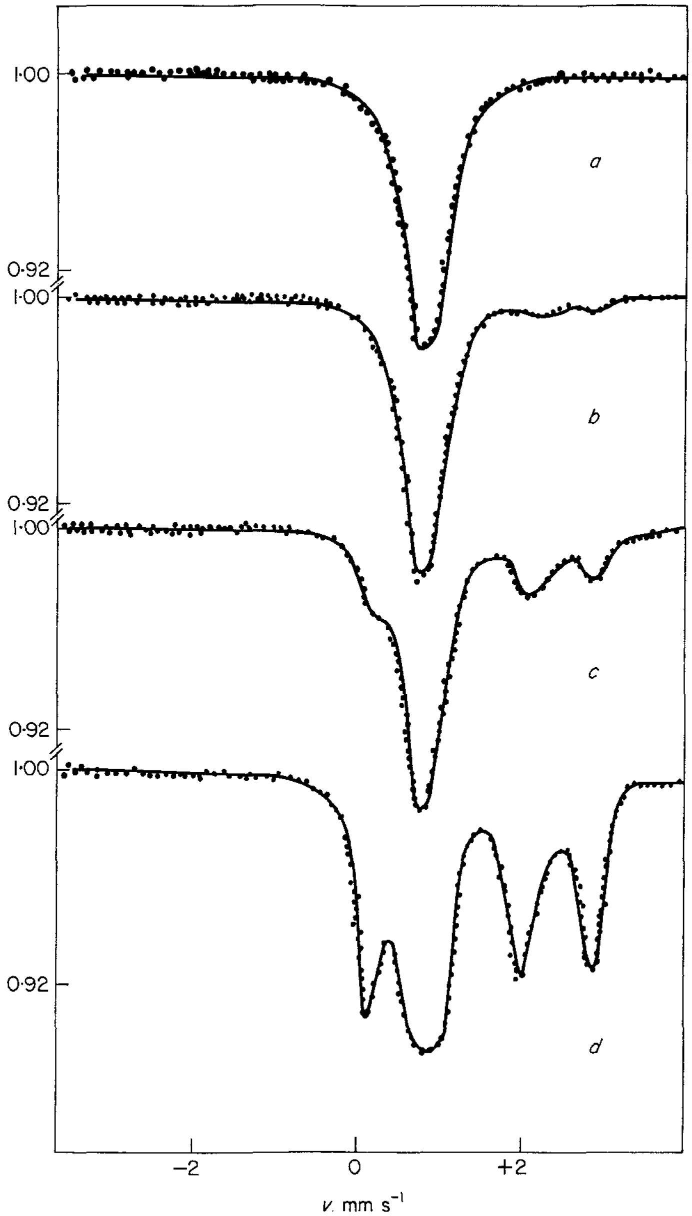

Figure 6. Mossbauer spectra of the Co–Mo–Bi–Fe oxide catalyst before (*a*) and after reduction with propylene at 270°C (*b*), 350°C (*c*), and 390°C (*d*) (Firsova *et al.* 1986b).

spectroscopy (Firsova *et al.* 1986). Figure 6 presents Mössbauer spectra of the initial Co–Mo–Bi–Fe catalyst (*a*) and of the same specimen after its reduction at different temperatures (*b*)–(*d*) (Firsova *et al.* 1986). In its oxidized state Fe is in the form of crystalline $Fe_2(MoO_4)_3$ with a chemical shift $E_1 = 0{\cdot}68 \pm 0{\cdot}01$ mm s^{-1}. After treatment of this catalyst with C_3H_6 it reduces in part to β-$FeMoO_4$. As seen from figure 6 the extent of reduction defined as $Fe^{2+}/Fe^{2+} + Fe^{3+}$ greatly increases with temperature. At 270°C it is 0·14, at 350°C 0·44, and at 390°C 0·76. The amount of oxygen removed

Table 5. The amount of oxygen (n_0) removed from the catalysts by reduction of 40 pulses i-C_4H_8 (Firsova *et al.* 1986b).

Catalyst	T(°C)	n_0 (at $g^{-1}(\times 10^{19})$) Kinetic results	n_0 (at $g^{-1}(\times 10^{19})$) GR spectra results
Co–Mo–Bi–Fe	270	2·2	2·5
	350	7·0	8·0
	390	11·0	13·0

from the lattice by reduction of $Fe_2(MoO_4)_3$ to $FeMoO_4$ has been calculated from spectrometric data. These results were compared with those obtained in a microcatalytic reactor under the same conditions (Table 5).

It will be seen from Table 5 that oxygen withdrawn by reduction of the Co–Mo–Bi–Fe comes almost completely from the Fe molybdate. After reoxidation of the Co–Mo–Bi–Fe catalyst, its Mössbauer spectra appeared to be identical to the initial ones.

From quantitative results obtained in this work it follows that the removal of oxygen from Fe molybdate to form $FeMoO_4$ and anionic vacancies occurs as follows:

$$Fe_2(MoO_4)_3 \xrightarrow{\text{reduction}} \{2\ FeMoO_3)\}\square_x + X[0]$$

where □ stands for the anionic vacancy.

As stated in a monograph by Krylov (1986) the ionization of vacancies leads to an excess negative charge and a redistribution of the electron density takes place over the whole iron molybdate crystal causing reduction of the latter. Consequently, modification of the Co–Mo catalyst with Fe results in the formation of iron molybdate which supplies oxygen for selective oxidation of hydrocarbons.

The oxygen mobility is not the only factor responsible for oxidation. Together with oxygen removal from the lattice, the hydrocarbon induces changes in the valences of the catalyst metal ions. The organic oxidation mechanism is known to involve several stages. One is the adsorption of the oxidized molecule on the catalyst to form various surface complexes (π- and σ-allylic for olefins). This is accompanied by changes in valence of the catalyst metal ions. The introduction of additives into oxide catalysts either induces the formation of other complexing centres or facilitates electron transfer between various ions of the catalyst and the reactants to form a charge transfer complex M_1–O–M_2.

The interaction of Fe and Te introduced into $CoMoO_4$ with the reaction components (oxidation of C_3H_6 to C_3H_4O) has been studied by Mössbauer spectroscopy (Firsova *et al.* 1974). The catalytic activity of the modified catalyst and its selectivity for C_3H_6 oxidation to C_3H_4O rises several times (table 6). It follows from spectrometric results that on introduction of additives new compounds are produced in the oxide catalyst, $Fe_2(MoO_4)_3$ and $CoTeO_4$. Their interaction with the reactant mixture changes in part the oxidation states of Fe and Te (table 7).

The changes in Fe and Te valences provide evidence that the additives not only act on the structure, but also enhance the electronic interaction between the catalyst ions and the reactants, thus lowering the energy of the Me–O–Mo charge transfer (Me stands for a cation in the molybdate lattice), and this improves the process selectivity.

Table 6. The dependance of additives Fe and Te on the Co–Mo catalyst activity and changes in valence of catalyst metal ions. (Firsova *et al.* 1974).

Additive	Changes of valence	Conversion C_3H_6 (%)	Selectivity in C_3H_4O (%)
—		10	10
Fe	$Fe^{3+} \rightarrow Fe^{2+}$	63	35
Te	$Te^{6+} \rightarrow Te^{4+}$	55	30
Fe+Te	$Fe^{3+} \rightarrow Fe^{2+}$ $Te^{6+} \rightarrow Te^{4+}$	72	44

Table 7. The rate (V_{red}) and the extent (n_0) of the catalysts, reduction by i-C_4H_8 (Firsova *et al.* 1986a).

Catalyst	Conversion i-C_4H_8 (%)	Selectivity in C_4H_6O (%)	n_0 after 10 pulses (at m^{-2})	v_{red} (μmol m^{-2} s^{-1})	
				initial	after 5 pulses
Co–Mo–Bi–Fe	57	40	$2{\cdot}7 \times 10^{18}$	0·62	0·05
Co–Mo–Bi–Fe–K	76	83	$1{\cdot}8 \times 10^{19}$	0·70	0·80

Iron ions introduced into catalytic systems considerably improve the performance. The mechanism of the effect of iron ions on the Co–Mo–Bi oxide system has been discussed above. It appears that iron ions change the generation rates of partial oxidation products and suppress side-processes also in other systems such as Sn–Mo (Alkhazov and Margolis 1988) (figure 7).

Analysis of experimental results showed that modification induces various interrelated processes, such as structure rearrangement and electronic interactions between catalyst components (Krylov 1986). Both exert an effect on the catalyst activity and the process selectivity.

4. Modification of catalysts by acid–base additives

4.1. *Oxide systems*

Much evidence has been reported concering the effect of alkaline additives on various catalytic reactions (see e.g. the review by Mross 1983). The trivial interpretation of this effect for various catalysts (metals and oxides) is that associated with the acid–base properties of solid surfaces and the reactants. The alkaline and acidic properties of reaction products and the strength of their bonding to the surface (Golodets 1982) are taken to be the factors responsible for catalytic activity.

In his monograph Golodets (1982) states that, for a V–Mo oxide system in the oxidation of benzene to maleic anhydride (MA), both Na and P ions in the catalyst improve the process selectivity. These addititives do not seem to have an effect only on the acid–base properties of the catalyst surface. EPR results showed that in the presence of Na and P the amount of V ions in the catalyst increases, and in the close-to-surface layer, as found by XPS there is a change in the Mo^{6+} to V^{4+} ratio.

The Na, K, Rb, Cs ions in the V–Ti catalyst for *o*-xylene oxidation to phthalic anhydride (PhA) improve the process selectivity due to the lower rate of PhA reoxidation. It increases up to 87% with growing electronegativity of the alkali metal ions (Il'inich and Ivanov 1983). All alkaline additives stabilize the oxidized state of V in the V–Ti catalyst and neutralize the acidic sites of the surface.

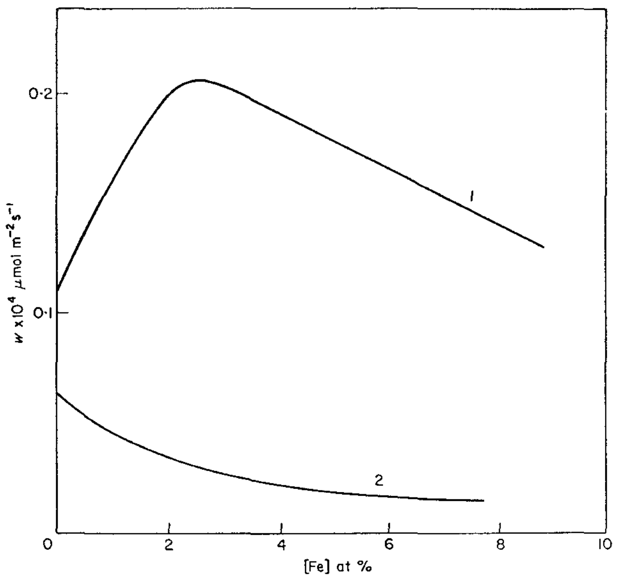

Figure 7. The formation rate of acetone (1) and carbon dioxide (2) as a function of Fe content in propylene oxidation over the Sn–Mo oxide catalyst at 200°C (Alkhazov and Margolis 1988).

The addition of K ions to the Sn–Mo–Fe system for oxidation of propylene to acetone raises the selectivity from 23 to 94% on account of the lower rate of total oxidation. In the presence of K ions the amount of the reduced Mo form increases on interaction with propylene.

The effect of alkaline additives (Li, Na, K) and of alkaline earth elements (Mg, Ca, Ba) on the activity of a butane oxidation catalyst, and of a MA V–P catalyst has been studied by Zazhigalov *et al.* (1988). No connection was observed between the surface acidic properties and the rate of butane oxidation, but the energy of oxygen bond in the lattice and the catalytic activity were found to change with modification. The mechanism of alkaline additives action was studied in greater detail for the Co–Mo–Bi–Fe catalyst in the partial oxidation of olefins to unsatruated hydrocarbons.

It has been found that modification of a Co–Mo–Bi–Fe catalyst by alkaline additives (Li, Na, K, Cs) caused no changes in the acid–base properties of the catalyst surface. However, by means of modern physical methods (e.g. Mossbauer spectroscopy, EPR, XPS), it was shown that the alkaline elements have an effect on the catalyst structure. A modified Co–Mo–Bi–Fe catalyst contains $Fe_2(MoO_4)_3$ of a garnet structure with a vacant dodecahedral sublattice. Upon addition of the alkaline elements, particularly of K with its ion radius optimal in respect to this structure, the vacant sublattice becomes partly filled. The defective nature of $Fe_2(MoO_4)_3$ increases and its structure transforms into that of a non-stoichiometric garnet containing oxygen vacancies

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

where $\square^\circ$ stands for a vacancy in the dodecahedral sublattice, $\square^-$ is an oxygen anionic vacancy.

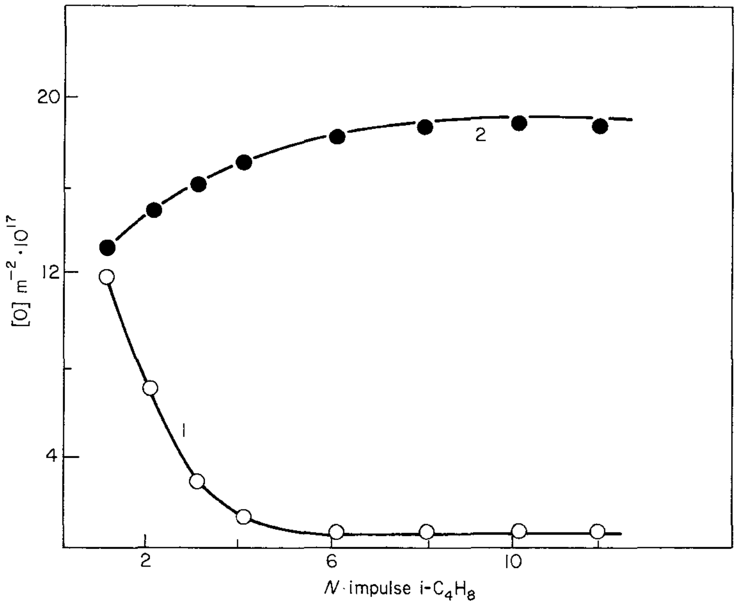

Figure 8. Amount of O_2 (n_0) reacting in every i-C_4H_8 pulse in the Co–Mo–Bi–Fe (1) and Co–Mo–Bi–Fe–K (2) catalysts (Firsova *et al.* 1986a).

Such structural changes have a marked effect also on the mobility of the lattice oxygen. Modification of the Co–Mo–Bi–Fe catalyst by K enhances the conversion and selectivity of i-C_4H_8 oxidation into C_4H_6O. To find out the effect of modification on the catalyst oxygen mobility its reduction with i-C_4H_8 has been studied by a kinetic method and Mössbauer spectroscopy (Firsova *et al.* 1986a).

Figure 8 shows the variations in the amount of oxygen reacting with every 2 ml of i-C_4H_8 pulse in catalysts containing (curve 2) and not containing (curve 1) K. The i-C_4H_8 conversion over a modified catalyst does not fall from pulse to pulse, but increases and becomes constant after 8–10 pulses. A drop in i-C_4H_8 conversion becomes apparent only after reduction with 25–30 pulses.

The reduction rate of the catalyst modified by K is also higher. This is particularly evident after interaction with 3–4 pulses of i-C_4H_8: the rate of Co–Mo–Bi–Fe catalyst reduction decreases by a factor of almost ten, whereas that of Co–Mo–Bi–Fe–K slightly increases (table 7). The extent of the modified catalyst reduction, that is, the amount of oxygen removed by interaction in an equal number of olefin pulses is almost an order higher than that of a catalyst with no K (Firsova *et al.* 1968a).

Analysis of the Mössbauer spectra and their correlation with kinetic data obtained in a microcatalytic reactor show that reduction occurs mostly via the lattice oxygen of $Fe_2(MoO_4)_3$. In the presence of K the oxygen mobility increases just in this lattice, as seen from spectra of the reduced samples. The reduction extent of the Co–Mo–Bi–Fe and Co–Mo–Bi–Fe–K specimens, calculated from the ratio of normalized areas under the Fe^{2+} molybdate spectra and the total spectral areas of the $Fe^{2+}+Fe^{3+}$ molybdates, is 0·12 and 0·75 respectively.

Modification of the Co–Mo–Bi–Fe catalyst by acidic additives, such as phosphorus, markedly suppresses its activity (Firsova *et al.* 1986b). The C_3H_6 conversion falls from 87 to 14% and the selectivity of oxidation to acrolein from 60 to 32%.

Both P and K were found to have virtually no effect on the acid–base properties of the catalyst surface. As shown by X-ray analysis and Mössbauer spectroscopy, the presence of P in the catalyst composition hinders the formation of crystalline $Fe_2(MoO_4)_3$. The rate and extent of the Co–Mo–Bi–Fe–P catalyst reduction with C_3H_6 are an order lower than those for Co–Mo–Bi–Fe.

Thus, the changes in catalytic characteristics of oxide systems modified by alkaline and acidic elements often are a function of the acid–base properties of the catalyst surface (Ai 1978). But as shown above the additives also act on the solid structure and the mobility of reactive oxygen. Consequently both the acid–base surface properties and the structural changes have to be taken into account.

4.2. *Silver catalyst*

In addition to the oxides described above, metallic silver is used for partial oxidation of ethylene to ethylene oxide. The characteristics of this process have been discussed in many papers (Margolis 1977, Alkhazov and Margolis 1988, van Santen and Kuipers 1987) which deal with the mechanism of C_2H_4O formation, the nature of the catalyst surface, and the kind of bound oxygen. The silver modification principle is widely applied in the production of active and selective catalysts. Acid–alkali additives (K, Cs, Cl, Se) are most often used.

In a review by Kilty and Sachtler (1974) the mechanism of oxygen interaction with Ag is given as

1. $O_2 + Ag \rightarrow O^-_{2(ads)} + Ag^+$
2. $O_2 + 4Ag$ (atom assembly) $\rightarrow 2\ O^-_{(ads)} + 4Ag^+$
3. $O_2 + 4Ag$ (individual atoms) $\rightarrow 2\ O^{2-}_{(ads)} + 4Ag$ (assembly)

It was suggested (Grant and Lambert 1984, 1985a) that individual Ag atoms adsorb oxygen in a molecular form which is involved in C_2H_4 oxidation to C_2H_4O. CO_2 is produced by interaction of atomic oxygen adsorbed on four-atom Ag assemblies with C_2H_4. Another viewpoint is proposed by van Santen and de Groot (1986) who argue that C_2H_4 is formed also via atomic oxygen. Alkali- and halogen-containing additives are introduced into the catalyst in order to improve its activity and selectivity.

Studies of the effect of alkali ions positioned at various faces of Ag single crystals using modern spectroscopic methods showed that the alkaline additives enhanced the recombination rate of atomic to molecular oxygen, resulting in higher coverage of Ag with molecular oxygen. For instance, a surface structure involving oxygen has been observed on Ag (111) containing Cs ions (Campbell 1985). Ethylene oxidation over such a sample showed that Cs suppressed the rate of total oxidation and changed the activation energy of CO generation.

The modification of Ag by Cs ions changes not only the surface oxygen concentration, but also the rate of C_2H_4O isomerization (Grant and Lambert 1985b). Goddard and Lambert (1981) found that in the presence of Rb^+ ions molecular oxygen generation on Ag was due to peroxide formation by reactions

1. $2Rb_2O_4 \rightarrow 2\ Rb_2O + 3\ O_2$
2. $2Rb_2O \rightarrow O_2 + 4\ Rb$

Potassium ions deposited on Ag (110) alter the oxygen coverage which results in the formation of K_2O_4 that decomposes by the same mechanism as for Rb (Kitson and Lambert 1981).

The deposition of alkali ions on Ag alters the ratio of C_2H_4O to CO_2 formation rates in C_2H_4 oxidation, as well as the activation energies of these reactions, thus changing the process selectivity (Campbell 1985).

It was found (Tan *et al.* 1986) that the deposition of Cl ions on Ag(111) resulted in removal of the pre-adsorbed oxygen atoms. A characteristic modification curve for surface coverage by Cl was obtained. Changes in the kinetic parameters: the reaction rate and order, the activation energy of C_2H_4O and CO_2 generation have also been observed. According to Campbell and Koel (1985) Cl ions form a surface structure involving Ag ions. Adsorption of Cl ions enhances the diffusion of oxygen atoms into the Ag lattice (Ayyoob and Hegde 1986).

The modification of Ag by Cl is often realized by addition of $C_2H_4Cl_2$ to the reactant mixture. Roginskii (1947) called this procedure ‘gaseous modification’. Its mechanism is the same as that of the additives effect. Margolis (1977) found that $C_2H_4Cl_2$ dissociated on Ag surface to form AgCl. The deposition of ^{36}Cl on Ag results in the formation of AgCl and in the presence of the reactants this compound is reduced to form Cl^- ions. At 330°C the latter do not migrate over the metal lattice, but remain on the surface. Similar results have been observed for ^{131}I.

The modification of Ag by $C_2H_4Cl_2$ involves conversion of the latter according to the following mechanism:

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

Petrov *et al.* (1986) found that $C_2H_4Cl_2$ added to a $C_2H_4 + O_2$ mixture inhibited oxygen dissociation over Ag. The $C_2H_4Cl_2$ concentration enters into the kinetic equation for this process.

Table 8 lists the results obtained for the effect of alkali and halogen ions on the state of oxygen and its reactions at the Ag surface.

The modification of Ag catalyst influences not only the state of adsorbed oxygen, but also C_2H_4 adsorption. Ethylene was found to adsorb only in the presence of oxygen at the Ag surface.

Surface complexes are formed on interaction of C_2H_4 with oxygen. Their structure was studied by IR spectroscopy (Forse and Bell 1975a, b). As found earlier from measurements of the electron work function $\Delta\phi$ (Margolis 1977), the absorbed C_2H_4

Table 8. Effect of modifying additives on interaction with Ag.

Additives	Modification characteristics
K^+ Rb^+ Cs^+	Increase: of O_2 chemisorption; Formation of peroxides $2Me_2O_4 \rightarrow 2Me_2O + 3O_2$ (O_2 generation); Increase of recombination rate $2O^- \rightarrow O_2$; Change in isomerization rate of C_2H_4O; Changes in kinetic parameters of C_2H_4 oxidation
Cl^-	Decrease: Dissociation $O_2 \rightarrow 2O$ and weakening of bond energy $Ag \rightarrow (O^-)$. Increase of desorption and recombination rates of O atoms. Increase of O diffusion into the Ag lattice. Displacement of O^- from the Ag surface. Changes in kinetic parameters of oxidation.

becomes positively charged, but the surface potential is governed by the negatively charged oxygen. The positively or negatively charged additives (alkaline elements and halogens respectively) adsorbed on Ag, change the energies of oxygen and ethylene–oxygen complexes bonding with the surface, as well as the heat of oxygen adsorption. Such an electronic factor must probably act on the activation energies for partial and total C_2H_4 oxidation. The combined adsorption of K and Cl on Ag (100) has been studied by Bowker *et al.* (1987). Electrostatic interaction between Cl and K ions was found to occur. AgCl stabilized by K^+ ions is formed on the surface. KCl desorbing at 700 K was also detected.

Thus, just as for oxide systems, the acid–alkali additives on silver mostly change not the acid–base properties of the surface, but the forms of oxygen adsorbed by the metal, as well as the kinetic characteristics of ethylene oxidation to ethylene oxide.

5. Conclusions

Catalyst modification by additives is very often encountered in catalytic oxidation processes; and selectivity of these processes may be regulated by certain additives when administered in optimal concentrations.

The concept of 'modification' is now widely adapted. Modification also provides the possibility of changing the surface state, for instance in order to replace the OH groups in silica gel by certain other elements, to deposit various complexes and molecules on the catalyst surface, etc.

It was reported (Somorjai 1987) that the modification of simple and complex catalytic systems induces changes in the structure in the bulk and at the surface of a solid as well as in bond energies on adsorption of reactants. The polyfunctionality of modified systems was noted and it was suggested that a monitoring of their structure would be conducive for selectivity control.

Before the modification phenomenon was discovered, all catalytic systems were classified as promoted and complex. The range of concentrations of additives in the system was taken as a criterion of such a distinction. Analysis of the present data on the action of additives in various crystals shows that the distinction between the two groups is conditional. As described above, the additives may be dissolved in the basic matrix to form a solid solution (monophase system) or some new compounds (multiphase system). It was found by using the present physico-chemical methods that even very small amounts of additives can induce the formation of new compounds, and consequently all the available catalysts are in fact multicomponent or multiphase.

Since the modified catalysts were found to be multiphase, it was suggested that their functions were partitioned between phases (Krylov 1986, Krylov and Margolis 1983, Krylov *et al.* 1985). This can be exemplified by propylene oxidation over a Bi and Fe modified Co–Mo oxide catalyst consisting of Co, Bi and Fe molybdates. In the course of stationary propylene oxidation the Fe^{3+} molybdate partially reduces to $FeMoO_4$ and a super-equilibrium concentration of vacancies occurs at their boundary. By diffusing to the interphase surface $Fe_2(MoO_3)/\beta$-$FeMoO_4$ can act as sites of dissociative oxygen adsorption from the gas phase to form lattice oxygen. The transport of this oxygen to active surface sites where the olefin adsorbs and oxidizes is realized at the interphase between iron and bismuth molybdates.

A partially reduced $Fe_2(MoO_4)_3$ lattice with an elevated concentration of defects forms under reaction conditions. It represents a 'transport artery' for delivery of the required oxygen to the catalyst active sites where oxidation occurs. (This is the essence of the so-called sacrificial oxygen concept that lies at the heart of the uniform selective oxidation catalysts described by Thomas (1988) and Thomas *et al.* (1989)). The transitions of iron molybdate $Fe_2(MoO_4)_3 \rightleftarrows \beta$-$FeMoO_4$ are facilitated by the presence of the basic matrix of the iso-structural phase β-$CoMoO_4$, since the interphases β-$FeMoO_4$ and β-$CoMoO_4$ are coherent and, on condition of a sufficient number of anionic vacancies, $FeMoO_4$ generation occurs with virtually no energy barrier.

It was found (by spectrometry) that additives tend to migrate from the bulk to the surface forming a new individual phase. This indicates that the catalyst represents a multiphase, rather than a monophase system.

The modification effect is particularly evident in the presence of alkali elements that create new main sites at the catalyst surface. On the one hand, these sites yield new compounds (for instance salts) or for vanadium catalysts, bronzes, thus increasing the number of phases in the catalyst structure. Alkali elements can become incorporated into the system and contribute to its rearrangement (e.g. in the presence of K^+ ions the garnet structure of iron molybdate converts into a non-stoichiometric one with a large number of defects). All these changes caused by alkali additives have an effect on the oxygen state in these systems. To ensure high selectivity in partial catalytic oxidation total oxidation has to be suppressed. Different forms of oxygen—molecular, atomic and oxide lattice oxygen—are known to be involved both in total and partial oxidation. For silver, an alkali additive stimulates surface formation of peroxides that decompose to form atomic oxygen which rapidly recombines to molecular oxygen in the presence of this additive. On the other hand, such additives lower the atomic oxygen amount and accordingly the rate of total ethylene oxidation.

When hydrocarbons are converted over oxide catalysts, modification by alkali elements causes a change in the nucleophilic oxygen to electrophilic ratio (Sokolovskii 1986). It was suggested that these forms are involved in the oxidation. The additives regulate the amounts of such oxygen forms at oxide surfaces.

The multifunctional effect of alkali elements on the catalyst activity is now widely applied for production of effective catalysts. Phosphorus and halogens are other additives introduced into oxide catalysts. The effect of these elements, just as of the alkali additives, is connected with the changes in properties of different forms of oxygen, the appearance of new active sites at the catalyst surface, and their effect on structure. The changes in surface coverage with different forms of oxygen is often due to the electronegativity of acidic additives.

When ethylene is oxidized over silver, the Cl ions introduced into silver or added to the reactant gas mixture as dichloroethane represent the basic element capable of markedly lowering the total oxidation rate. The action of this additive on the concentration of the surface atomic oxygen is responsible for the mechanism of the halogen effect.

The addition of phosphorus to oxide systems can change not only the acidic properties of the surface, but also the catalyst structure. For instance phosphorus added to a Co–Mo–Bi–Fe catalyst (see above) hinders the formation of the tervalent iron molybdate structure and in this way deprives the catalyst of its main 'oxygen pump' that ensures propylene oxidation.

In this paper most attention is paid to the promoting action of additives and to its mechanism. However, with a higher additive concentration, the reaction rate decreases and their is change in the activation energy. The mechanism of such 'poisoning' is less clear and insufficiently studied. A higher concentration of additive results in increased generation of new compounds in the system. These compounds usually are of low activity, and the number of active sites becomes smaller in their presence. For instance with an increase in the amount of iron ions in the Co–Mo–Bi–Fe system there appears, besides molybdate, an iron oxide on which propylene is converted into total oxidation products and the selectivity of acrolein formation from olefin markedly drops. Such a process is particularly characteristic of solid solutions, where an increase in the amount of additive results in the appearance of a solubility limit and the phase inactive for the given process falls out. This was observed for iron ions introduced into a Sn–Mo catalyst.

When the additive amount is higher than optimal for the given reaction, large clusters of the catalyst elements and the additive can be formed (Krylov 1986). The bonding energy of oxygen adsorption on these clusters is lower and the total oxidation rate becomes higher, whereas the selectivity of partial oxidation drops.

Electron transport between ions involved in the catalyst composition occurs in catalytic oxidation. An optimal concentration of additive favours the transport, since it creates a new, more advantageous, lattice structure. An above optimal concentration can disturb the insertion of the ions and form electron traps. The rates of individual reactions become lower and the catalyst becomes poisoned.

Thus, the modification of various catalytic systems results in formation of new compounds in the bulk and at the surface of the catalyst there occur changes in the number and composition of active sites, in the solid structure, in its ability to rearrange, and in the electronic interactions between the catalyst elements. Additives exert an effect on the kinetic regularities (reaction rate, activation energy) and on the reaction mechanism (structure of surface compounds, bond energy with the surface).

The multifunctionality of various additives hampers the formulation of theories that predict their effects. But accumulated experience of known trends combined with a thorough analysis of the effect of the additive permit effective catalysts for oxidation of various organic compounds to be prepared.

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