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Mechanism of heterogeneous catalytic oxidation of organic compounds to carboxylic acids †

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The results of studies on the mechanism of heterogeneous catalytic oxidation of organic compounds of different chemical structure to carboxylic acids are analyzed and generalized. The concept developed by Academician G.K.Boreskov, according to which the direction of the reaction is governed by the structure and bond energy of surface intermediates, was confirmed taking the title processes as examples. Quantitative criteria of the bond energies of surface compounds of oxidizable reactants, reaction products and oxygen that determine the selective course of the reaction are presented. The bibliography includes 195 references.

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1. Introduction

Selective oxidation of organic compounds is widely used in industrial catalysis.[1–3] High demand for this area gave an impetus to intensive basic research into the mechanism of reactions, catalytic action and design of catalysts.[4–8] Numerous studies on the mechanism of heterogeneous catalytic oxidation of various organic compounds to oxygen-containing products (alcohols, aldehydes, ketones, acid anhydrides) made it possible to formulate the principal conditions for selective course of these reactions,[9–12] namely, weak bonding between the catalyst and oxidizable substances and products of partial oxidation and strong bonding between the catalyst and oxygen.

Initially, the emphasis was placed on the state of oxygen. A large series of studies carried out under the guidance of Academician G.K.Boreskov is devoted to research into the mechanism of oxidative catalysis. The results obtained were summarized in reviews.[13–16] They illustrated the Mars–Van Krevelen redox mechanism[17] and demonstrated quantitative dependences of the activity of catalysts on the bond energy of oxygen in the deep oxidation reactions in the form of the Brønsted–Polanyi equation

$$\Delta E = \pm\alpha\,\Delta q \qquad (1)$$

where ΔE is the change in the activation energy, α is a constant and Δq is the change in the heat of adsorption of oxygen.

Experimental data[13–16] fall on the right branch of the so-called volcano curve (see below)[18–20] and characterize the dependence of the catalyst activity on the binding energy of oxygen in the rate-limiting step, *viz.*, oxygen abstraction from oxide.[21] The same value of the coeffcient $\alpha = 0.5$ for all reactions demonstrates that activation of the oxidizable reactant is of no consequence in the deep oxidation reactions.

A selective reaction requires a strongly bound oxygen; however, according to Boreskov, the key role is played by the specific interaction between the oxidizable substance and the catalyst.[22–24] The term 'specific' implies the ability of the catalyst to generate a surface compound of a particular structure, which is rather weakly bound to the

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† In memoriam of Academician Georgiy Konstantinovich Boreskov on the occasion of his 110th birthday.

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active site. 'Establishing the reasons for this specifity and its dependence on the character of the interaction between the oxidizable substance and the catalyst is the high-priority task for the theory of selective oxidation.'[24] To solve the problem, the authors of this review carried out a series of studies on the mechanism of oxidation of organic compounds of different nature to carboxylic acids.

Carboxylic acids are an important and abundant class of organic compounds.[25,26] Some of them are used as food products (*e.g.*, acetic, butyric and citric acids) or pharmaceuticals (*e.g.*, nicotinic, ascorbic, succinic and acetylsalicylic acids). Large amounts of carboxylic acids are used in chemical industry for production of plastics, polymers, synthetic fibres, fragrances, insecticides, as well as in consumer goods, food and pharmaceutical industries. Carboxylic acids are traditionally synthesized in the liquid phase; however, there has been considerable research activity aimed at developing methods of gas-phase synthesis of carboxylic acids on solid catalysts.

Nippon Shokubai (Japan) pioneered in production of acrylic acid by oxidation of propylene in the late 1960s. In China, nicotinic acid is commercially produced by the oxidation of β-picoline.[27] The development of a technology for the oxidation of propane to acrylic acid began in the early 1990s.[28] Gas-phase methods of heterogeneous catalytic oxidation of organic compounds to acetic, butyric and benzoic acids are also developed; however, the design of selective catalysts is a challenge. The last decade was marked by transition from empirical search for appropriate catalysts to the design of active sites based on the reaction mechanism. Ideologically, our studies are based on the concept of the chemical nature of catalysis developed by Academician G.K.Boreskov,[29] according to which the course of a reaction (selective or deep oxidation) is governed by the structure and binding energy of intermediate surface compounds.

Research into reaction mechanisms involves studies of surface complexes of organic substances of different chemical composition and nature (acrolein, formaldehyde, ethanol, isomeric picolines), oxidation products, reactivity of intermediates and the role of oxygen in their formation and transformations.

The main goal of this review is to illustrate the importance, topicality and validity of Boreskov's concept of catalysis for selective oxidation taking our results and published data as examples.

2. Surface complexes of oxidizable organic compounds

The mechanism of heterogeneous catalytic oxidation of acrolein, formaldehyde, ethanol, β-picoline and γ-picoline to acrylic, formic, acetic and isomeric pyridinecarboxylic (nicotinic, isonicotinic) acids, respectively, was studied.

The V–Mo oxide systems are highly selective in the oxidation of acrolein,[30,31] while the V–Ti oxide catalysts exhibit high selectivity in the oxidation of formaldehyde,[32,33] ethanol[34,35] and picolines[36–38] (Table 1). The yields of acids on these catalysts are more than 80% and the initial selectivity (at low conversions) is nearly 100%.

In situ vibrational spectroscopy is the main method for the determination of the molecular structure and reactivity of surface intermediates of heterogeneous catalytic reactions and, therefore, for investigation of reaction mechanisms on the molecular level.[5,39–41]

It is *in situ* IR spectroscopy that was used to identify the surface complexes of oxidizable reactants and to establish pathways of their conversion into reaction products, *viz.*, corresponding acids.

Surface compounds of acrolein and acrylic acid were studied in the temperature range of 25–300 °C. The IR spectra and structures of the surface compounds of acrolein on a V–Mo oxide catalyst are presented in Fig. 1. A thorough description of the experimental details, accurate assignment of absorption bands and identification of the surface compounds were reported in the literature.[42–46] At 25 °C, acrolein is adsorbed as coordinatively bound species (bands at 1370, 1625 and 1665 cm^{-1}). As temperature increases, this complex undergoes successive transformation into a carbonyl-bonded species (bands at 1625 and 1725 cm^{-1}) and then to surface acrylate (bands at 1445, 1520, 1630 cm^{-1}) and molecularly adsorbed acrylic acid (bands at 1630 and 1750 cm^{-1}).

Intermediates of the oxidation of formaldehyde on V–Ti oxide catalyst were studied in the temperature range of 70–200 °C (Fig. 2).[47–51] At temperatures below 100 °C, formaldehyde is mainly transformed into a dioxymethylene surface complex [$\delta(CH_2)$ = 1478 and 1411 cm^{-1}]. In the optimum temperature range (100–150 °C), this complex is transformed into oxidized structures with the carboxyl bond, namely, surface formates [$\nu_{as}(COO)$ = 1560 and 1668 cm^{-1}, $\nu_s(COO)$ = 1365 cm^{-1} and $\delta(C-H)$ = 1375 cm^{-1}] and adsorbed formic acid [($\nu(C{=}O)$ = 1720 cm^{-1}].

Table 1. Parameters of V–Ti oxide catalysts of oxidation of certain organic compounds.

Reaction	Catalyst composition (mass %)		s /m^2 g^{-1}	T/°C	Composition of initial mixture (mol.%) (see [a])	S (%)	X (%)	Ref.
	V_2O_5	TiO_2						
$CH_2O \longrightarrow HCOOH$	20	80	180	120	6.5 CH_2O + 8.0 H_2O	90	94	32
β-$C_5H_4NMe \longrightarrow C_5H_4NCOOH$	20	80	30	300	1.0 C_6H_7N + 20.0 H_2O	86	96	36
γ-$C_5H_4NMe \longrightarrow C_5H_4NCOOH$	20	80	63	250	1.0 C_6H_7N + 20.0 H_2O	85.8	85.6	38
$C_3H_4O \longrightarrow C_2H_3COOH$	12.5	87.5 [b]	80	260	4.0 C_3H_4O + 20.0 H_2O	98	92	31
$EtOH \longrightarrow MeCOOH$	10	90	153	220	5.0 EtOH	62	93	34

Note. Notations are as follows: s is the specific surface area, S is the selectivity to acid and X is the conversion of the initial compound.
[a] The rest is air. [b] V–Mo oxide catalyst, shown is the content of MoO_3.

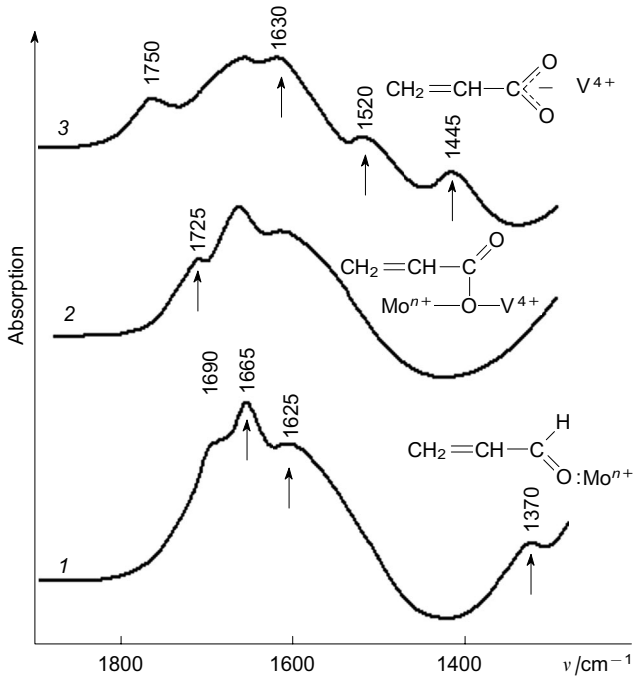


Figure 1. IR spectra and structures of surface compounds formed during the oxidation of acrolein on V–Mo oxide catalyst at 25 (*1*), 160 (*2*) and 280 °C (*3*). Adapted from Ref. 42.

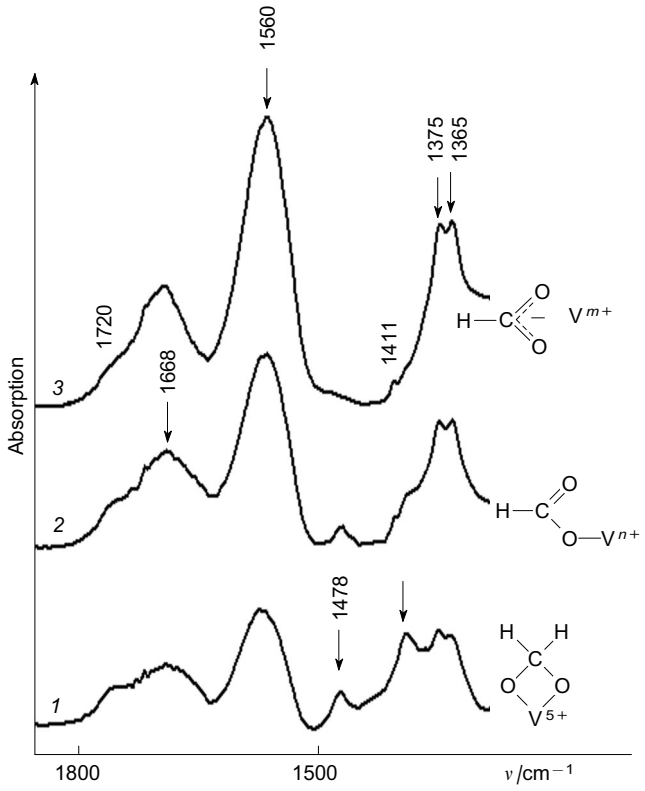


Figure 2. IR spectra and structures of surface compounds formed during the oxidation of formaldehyde on V–Ti oxide catalyst at 70 (*1*), 100 (*2*) and 120 °C (*3*). Adapted from Ref. 48.

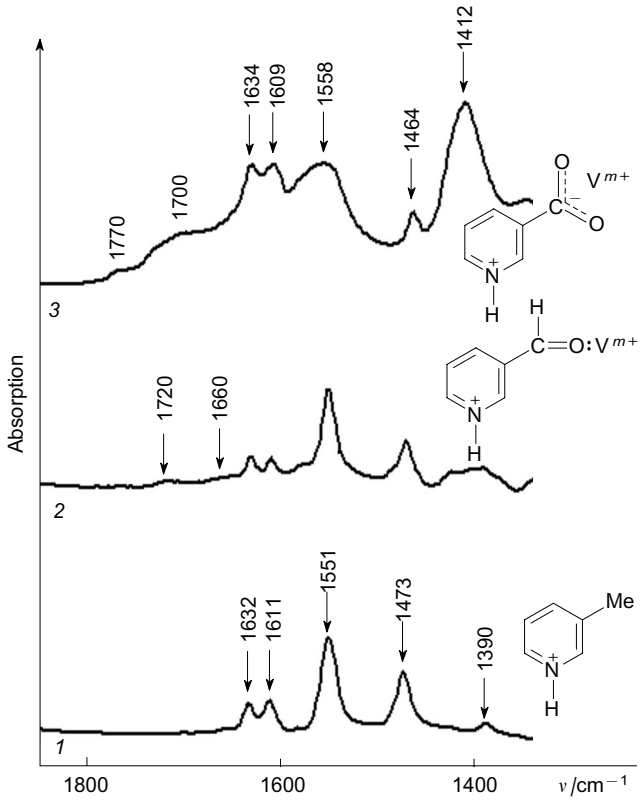


Figure 3. IR spectra and structures of surface compounds formed during the oxidation of β-picoline on V–Ti oxide catalyst at 120 (*1*), 160 (*2*) and 260 °C (*3*). Adapted from Ref. 55.

According to kinetic data,[36,52–55] the oxidation of β-picoline to nicotinic acid involves intermediate formation of pyridine-3-carbaldehyde. Adsorption of β-picoline at 120 °C (Fig. 3, spectrum *1*) is accompanied by the formation of a surface complex of the 3-methylpyridinium ion (bands at 1632, 1611, 1551, 1473 and 1390 cm^{-1}). In the temperature range of 150–220 °C (Fig. 3, spectrum *2*), C–H bonds in the picoline methyl group of dissociate and oxygen-containing aldehyde-like complexes are formed [ν(C=O) = 1720 and 1660 cm^{-1}]. As temperature further increases (Fig. 3, spectrum *3*), these complexes are converted into surface nicotinate (bands at 1634, 1609, 1558, 1464 and 1412 cm^{-1}) and products of the reaction, *viz.*, molecularly adsorbed [(ν(C=O) = 1730–1700 cm^{-1}] and gaseous [ν(C=O) = 1770 cm^{-1}] nicotinic acid.[50,53]

A study [54] on the adsorption of pyridine-3-carbaldehyde revealed the same processes as those observed in the case of β-picoline. Namely, at 120 °C, aldehyde exists as a coordinatively bound species. As temperature increases, it undergoes transformation into surface carboxylate and then molecularly adsorbed and gaseous nicotinic acid are formed in the optimum temperature range.

A similar order of reactions was also established for γ-picoline. The 4-methylpyridinium ion was consecutively converted into pyridine-4-carbaldehyde, isonicotinate and isonicotinic acid. It should be noted that these processes occurred at lower temperatures compared to transformations of β-picoline.[38]

The oxidation of ethanol in the temperature range of 100–230 °C affords acetaldehyde and acetic acid as major reaction products.[34,35]

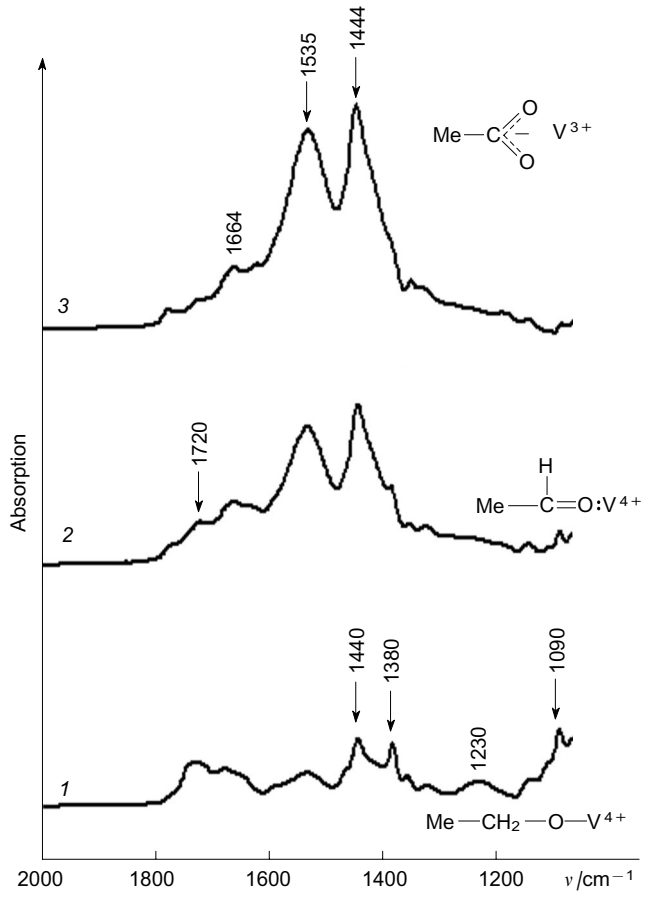


Figure 4. IR spectra and structures of surface compounds formed during the oxidation of ethanol on V–Ti oxide catalyst at 100 (*1*), 130 (*2*) and 150 °C (*3*). Adapted from Ref. 35.

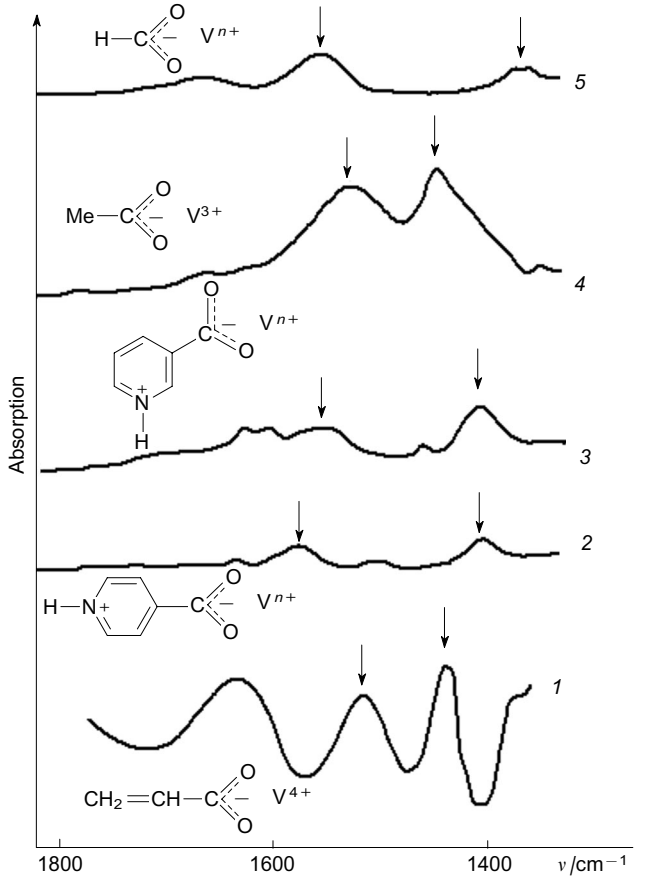


Figure 5. IR spectra of carboxylates: acrylate (*1*),[43] isonicotinate (*2*), nicotinate (*3*),[55] acetate (*4*) [34] and formate (*5*).[49]
The carboxylates formed upon adsorption of the corresponding acids on V–Mo (*1*) and V–Ti (*2*–*5*) oxide catalysts.

The IR spectra and structures of surface compounds formed by ethanol in the temperature range of 100–150 °C are shown in Fig. 4. At 100 °C (spectrum *1*), ethoxides (1440, 1380 and 1090 cm^{-1}) and molecularly adsorbed ethanol (1230 cm^{-1}) are mainly formed. In addition, the spectra measured at 100 °C exhibit bands of adsorbed acetaldehyde (1720 cm^{-1}). As temperature increases to 130 °C (spectrum *2*), the concentration of ethoxide decreases while that of adsorbed acetaldehyde increases. The bands of acetate (1535 and 1444 cm^{-1}) and adsorbed acetic acid (1664 cm^{-1}, spectrum *3*) also appear in the spectrum. The concentrations of these compounds increase and reach a maximum value at 180–200 °C (see Fig. 3 in Ref. 34).

The concentration of surface carboxylates formed during the oxidation of the organic compounds studied on V–Ti oxide catalysts in oxygen-free reaction medium is always much higher. In this case, carboxylic acids (formic, acetic and nicotinic acids) are not formed at all or their formation occurs at a noticeably lower rate (isonicotinic acid).

The IR spectra of acrylate, isonicotinate, nicotinate, acetate and formate formed during adsorption of corresponding carboxylic acids are presented in Fig. 5. The complexes identified during the oxidation of aldehydes, ethanol and β-picoline (see Figs 1–4) have the same spectral characteristics. The binding sites of carboxylates on the V–Ti and V–Mo oxide catalysts are vanadium cations.

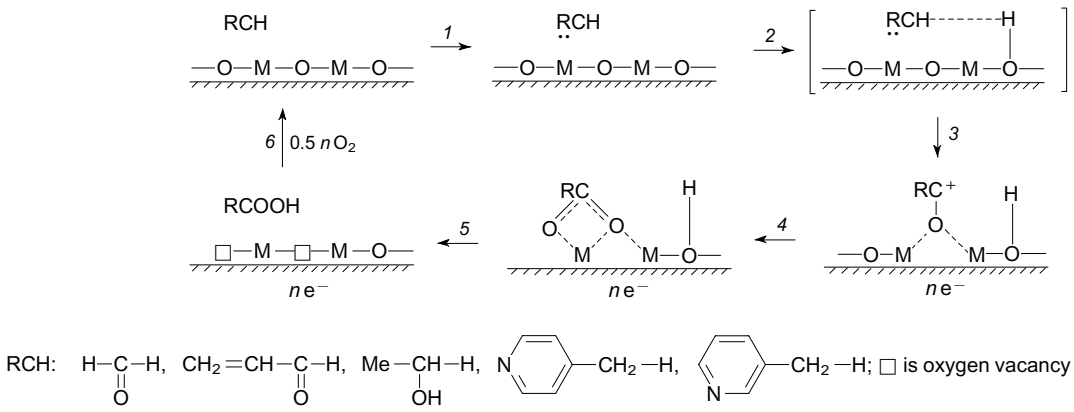
3. Formation of carboxylic acids: a generalized scheme

The formation of surface compounds and their transformations into reaction products obey a common pattern irrespective of the nature of catalysts and starting reactants, so the mechanism of formation of carboxylic acids can be described by Scheme 1, where R is the molecular fragment that remains untouched throughout the reaction and □ are oxygen vacancies.

Conversion of acrolein, formaldehyde, ethanol, β-picoline, γ-picoline and pyridinecarbaldehydes into acids involves the formation of certain surface intermediates. These intermediates are structurally similar and their transformations follow identical pathways. In all cases, the following main stages occur consecutively:

— formation of molecularly adsorbed compounds as a result of interaction between the initial molecule and the active site of the catalyst *via* the atom with increased electron density (oxygen atom in aldehyde and alcohol and nitrogen atom in pyridinecarbaldehydes, β-picoline and γ-picoline);

Scheme 1



— heterolytic dissociation of the C – H bond in the CHO group of aldehydes, CH_2OH group of the alcohol or in the Me group of picolines;

— oxidation of the hydrocarbon moiety accompanied by reduction of the active site,

— interaction of the oxidized moiety with the oxygen atom from the catalyst to give a carboxylate (formate, acrylate, acetate, nicotinate and isonicotinate) complex bound to the reduced site;

— decomposition of the carboxylate and desorption of the corresponding acid,

— re-oxidation of the catalyst in a separate stage by the redox mechanism (in the case of acrolein oxidation) or by the associative mechanism during the combined stage involving oxygen adsorption and acid desorption (in the case of the oxidation of formaldehyde, pyridinecarbaldehyde, β-picoline, γ-picoline and ethanol).

If the initial molecules contain electron-rich heteroatoms, primary activation of these molecules on highly charged V^{5+} and Mo^{6+} cations is implied (stage *1* in Scheme 1). According to ^{51}V NMR spectroscopy data, the catalysts studied contain this type of vanadium cations in the distorted octahedral oxygen environment.[56, 57] Primary activation leads to formation of molecularly adsorbed structures. This step is also accompanied by polarization of the C – H bond, which favours the interaction of the heteroatom with the nucleophilic oxygen of the catalyst and subsequent heterolytic dissociation of C – H bonds (stage *2*). The negatively charged moiety thus formed reduces the active site (stage *3*), acquires a positive charge and reacts with oxygen atom of the catalyst to give (i) aldehyde-like and carboxylate structures in the case of heterocyclic compounds or (ii) carboxylates if the initial molecule, *e.g.*, formaldehyde or pyridine-3-carbaldehyde contains an oxygen atom (stage *4*). The oxygen-containing structures are bound to the reduced vanadium cations. Desorption of carboxylic acids leads to release of the reduced acive sites and oxygen vacancies for the Mars – Van Krevelen mechanism or the oxidized sites in the case of concerted redox mechanism (stage *5*). The oxidation state of vanadium in the reduced active sites (3+ or 4+) in the oxidation reactions (stage *6*) is discussed in the literature.[58 – 63]

The rates of formation and conversion of certain intermediates on different catalysts and in different reactions can differ appreciably, so some of them are difficult to observe under conventional experimental conditions; however, a common feature is the presence of surface carboxylates $RCOO^-$ bound to vanadium ions. Structurally, these salt-like surface compounds, *viz.*, formates, acrylates, acetates, nicotinates and isonicotinates resemble the corresponding acid anions and are the direct precursors of the acids.

The fact that the kinetic parameters of the decomposition of carboxylates match those of the formation of corresponding acids shows that it is the decomposition stage of the reactions under study that governs the collecting of the conversion of reactants to the products of selective or deep oxidation.

The rates of decomposition of formates and acrylates obtained under steady-state conditions in an IR cell during the oxidation of acrolein and formaldehyde, and the rates of accumulation of formic and acrylic acids in the gas phase (in oxygen or helium flow, respectively) are listed in Table 2. Experiments were carried out in an IR cell reactor and involved simultaneous collecting of IR spectra and measurements of product concentrations in the gas phase.[45, 51, 64] The decomposition of acrylate with the formation of acrylic acid occurred in helium flow[45, 64] while that of formate to give formic acid occurred in oxygen flow.[51] One can see that the rates of decomposition of the carboxylates and those of accumulation of the acids are close. Besides, the activation energy for the decomposition of formate, 25 kJ mol^{-1}, equals the energy measured in a separate kinetic experiment.[47] It follows that carboxylates are indeed the direct precursors of acids and their decomposition is the key stage of the formation of acids.

Various mechanisms of formation of acrylic acid or acrylonitrile from propane on oxide catalysts were pro-

Table 2. Rates (W) of decomposition of carboxylates and rates of formation of carboxylic acids on V – Ti and V – Mo oxide catalysts.

Catalyst	T/°C	$W \times 10^{-15}$/molecule m^{-2} s^{-1}	
		see [a]	see [b]
Reaction HCHO ⟶ HCOOH (*in oxygen flow*) (Ref. 51)			
V – Ti	100	3.1	2.9
	120	5.4	5.1
	130	6.9	6.7
Reaction CH_2=CH – CHO ⟶ CH_2=CH – COOH (*in helium flow*) (Ref. 45)			
V – Mo	190	0.9	1.1
	230	2.7	2.7

[a] Decomposition of carboxylate.
[b] Formation of carboxylic acid.

posed.[65–68] They have common stages, namely, activation and dissociation of the C–H bond, formation of a surface allylic complex and interaction with the catalyst oxygen to form an aldehyde-like complex whose subsequent transformation to acrylonitrile or acrylic acid depends on the chemical composition of the catalyst and on the reaction medium.

Grasselli *et al.*[65] proposed a network for oxidation of propane on a V–Mo–Te–Nb oxide catalyst *via* successive conversion of the surface complexes of propane with participation of lattice oxygen and re-oxidation of the catalyst by gaseous oxygen in accordance with the conventional Mars–Van Krevelen mechanism as the final step of the reaction cycle. A similar synthetic route to acrylic acid starting from propane *via* intermediate formation of surface acrolein and then acrylate was proposed by Trunschke.[66]

Vogel and co-workers[67] reported a mechanism for the oxidation of acrolein to acrylic acid on V–Mo–W oxide catalysts *via* conversion of the surface acetal into the surface acrylate and then into the acid. The surface complexes are formed with participation of the oxygen atom of the catalyst; oxidation of the reduced cations and filling of vacancies are accomplished by gaseous O_2 or bulk oxygen.[68] Acrylic acid can be formed from surface acrylate as a result of interaction with the neighbouring proton or displacement with water. We believe the latter path is also a possible route of conversion of surface formate on a V–Ti catalyst.[69, 70]

Takehira's research group reported a series of studies[71–75] on the mechanism of formation of nicotinic acid on promoted $CrVO_4$ catalysts. Their mechanism is analogous to that presented in Scheme 1. Intermediate surface aldehyde and nicotinate are formed with participation of lattice oxygen. The catalyst is oxidized by gaseous oxygen simultaneously with the desorption of aldehyde at a concerted stage (associative mechanism); nicotinate is formed on the oxidized active site and, in our opinion, it is weakly bound.

Hoelderich and co-workers[76–78] assumed that the oxidation of β-picoline to nicotinic acid on a V–Ti oxide catalyst proceeds by the Mars–Van Krevelen mechanism. The selective reaction requires a large excess of oxygen and water while the catalytically active species in this case are polymeric species $(VOx)_n$.

The mechanisms described above have a number of common features, *viz.*, participation of the lattice oxygen, the presence of consecutively converting oxygen-containing surface complexes and, finally, the presence of carboxylates as the acid precursors.

An alternative mechanism was also proposed.[79, 80] According to Schlögl,[79] lattice oxygen is not involved in the formation of intermediates and the key factor is the acid–base interaction of the surface fragments of the oxidizable reactants with hydroxyl groups of adsorbed water. Koltunov *et al.*[81] proposed a similar mechanism of acrylic acid formation. Namely, they considered an electrophilic-nucleophilic interaction of the surface complexes of acrolein with water which leads to incorporation of the second oxygen atom into the acyl group and thus formation of acrylic acid. This mechanism was also proposed for the formation of formic acid from methanol.[82]

By and large, the mechanisms suggested by Schlögl and Koltunov correspond to the mechanism of liquid-phase oxidation of organic reactants on supported metal catalysts,[83] according to which (i) the formation of acids from aldehydes as well as the formation of aldehydes from alcohols on Au, Pt and Pd catalysts involves the stage of adsorption of the reactants with the formation of metal alkoxide and (ii) hydrogen abstraction leads to formation of carbonyl species and a metal hydride. The reaction product is then formed with participation of OH groups that supply oxygen atoms to the alkoxy group and hydrogen to water. Oxygen favours removal of electrons from the metal surface and regeneration of hydroxide ions. These reactions proceed in liquid solvents at low temperatures under vigorous bubbling of oxygen.

We believe that the this mechanism is inapplicable to high-temperature reactions on oxide catalysts. The difference between the mechanisms is first of all determined by the chemical nature of the catalyst. The reaction on the oxide catalysts involves the M–O pair, whereas the lack of lattice oxygen in the reaction on metallic catalysts validates the involvement of water as oxygen supplier. The formation of acids on oxide catalysts does not require water in the reaction mixture. Acids are formed with 100% selectivity at low conversions (< 10%), no side products of deep oxidation and water are present, so the surface is completely dehydroxylated. In the absence of oxygen, the catalyst is less active and the reaction on the reduced catalyst results in other products, *viz.*, methyl formate for the oxidation of formaldehyde,[51] equimolar amounts of acetaldehyde and ethane[84] or carbon oxides[85] for the oxidation of ethanol and decomposition products for the oxidation of butane.[86]

Besides, liquid-phase oxidation on metallic catalysts and gas-phase oxidation on oxide catalysts result in different products. For instance, the oxidation of glycerol affords a mixture of tartronic, glycolic, oxalic and formic acids in the former case[83] and acrylic acid in the latter case.[87, 88]

In conclusion, mention may be made that the chemical nature of catalysts (metallic or oxide ones) plays a decisive role in catalysis, although the reaction conditions are also important. Reactions carried out under different conditions proceed by different mechanisms; however, mechanisms of the reactions conducted under identical conditions on same-type catalyst can differ only in details.

4. Mechanism of oxygen involvement

Scheme 1 shows that oxygen atoms of the catalyst are involved in at least two stages. Considering the oxidation of aldehyde and alcohol, these are the dissociation stage and the formation of oxygen-containing group (second oxygen atom is supplied to carboxylate from the oxidizable molecules). In the case of oxidation of isomeric picolines, the formation of carboxylates requires two oxygen atoms of the catalyst.

A steady state isotopic kinetic analysis (SSITKA) study[89] of $^{16}O_2$–$^{18}O_2$ isotopic exchange revealed the involvement of lattice oxygen in the synthesis of acrylic acid by the oxidation of acrolein. Characterization of this oxygen first of all requires the determination of the state of the catalyst under the reaction conditions. According to G.K.Boreskov,[90, 91] the catalyst and the reaction medium form a unified system, *viz.*, the catalyst influences the reaction medium, while the reaction medium changes the catalyst. 'Solid catalysts are labile components of a reaction system, so the chemical composition, surface structure and catalytic properties are changed under the influence of the reaction mixture. To each reaction mixture composition and temperature, there corresponds a certain state of a catalyst independent of its initial state'.[92] This was confirmed

experimentally taking catalysts of different composition in the oxidation of various organic compounds as examples.[93,94] In particular, *in situ* studies of the oxidation of acrolein demonstrated changes in the catalyst surface and in the bulk of the catalysts under the reaction conditions.[89,95]

Figures 6 *a*,*c* illustrate changes in the catalytic properties of a V–Mo oxide catalyst in the oxidation of acrolein upon stabilization of a steady state; Figs 6 *b*,*d* illustrate analogous changes in the absence of oxygen, *i.e.*, in the reduction of the catalyst with acrolein.[64,96] As the steady state is approached (see Fig. 6 *c*), the rate of deep oxidation decreases (curve *1*), the rate of selective oxidation to acrylic acid increases (curve *2*) and the selectivities vary correspondingly (see Fig. 6 *a*, curves *1* and *4*). The conversion of acrolein (curve *2*) increases. Low carbon balance (see curves *3* in Figs 6 *a*,*b*) in the initial stages of the catalytic reaction and reduction is indicative of the formation of strongly bound structures.

In the initial stages the reaction rates and selectivities vary in the same manner as they do in the reaction mixture with increasing extent of reduction of the catalyst (see Fig. 6 *b*); however, this is followed by fundamentally different behaviour of these parameters. The steady state is characterized by constant values of all parameters (plateau in all curves in Figs 6 *a*,*c*). The steady-state rates of catalysis and reduction are equal to each other at an extent of reduction of the catalyst monolayer of about 5% (shown by vertical arrows) and at a binding energy of oxygen of 250 kJ mol^{-1} (see curve *5* in Fig. 6 *b*). Equal values of the kinetic parameters for reduction and for catalysis point that transformation from completely oxidized to the steady-state catalyst under the reaction conditions occurs *via* reduction and is characterized by two main processes, *viz.*, removal of oxygen and a decrease in the extent of oxidation of cations. In the steady state, vanadium is reduced to the 4+ state.[96]

The energy state of oxygen can be assessed from the heats of adsorption measured calorimetrically.[97–99] The heat of adsorption of oxygen participating in the reaction was determined from the curves of reduction for the catalysts with relatively low-mobility oxygen (V–Mo–P, V–Mo–Cs). The heats of adsorption of catalysts with high-mobility oxygen (V–Mo and V–Mo–Cu) were determined *in situ* under the reaction conditions.[97,98] The heat of adsorption of oxygen on the V–Ti oxide catalyst was determined on the surface pre-reduced with carbon monoxide.[99] All the V–Mo oxide catalysts listed above are highly selective in the oxidation of acrolein to acrylic acid.[100,101] The V–Ti oxide catalyst is efficient in the oxidation of formaldehyde to formic acid[32,33] and in the oxidation of β-picoline and γ-picoline to nicotinic and

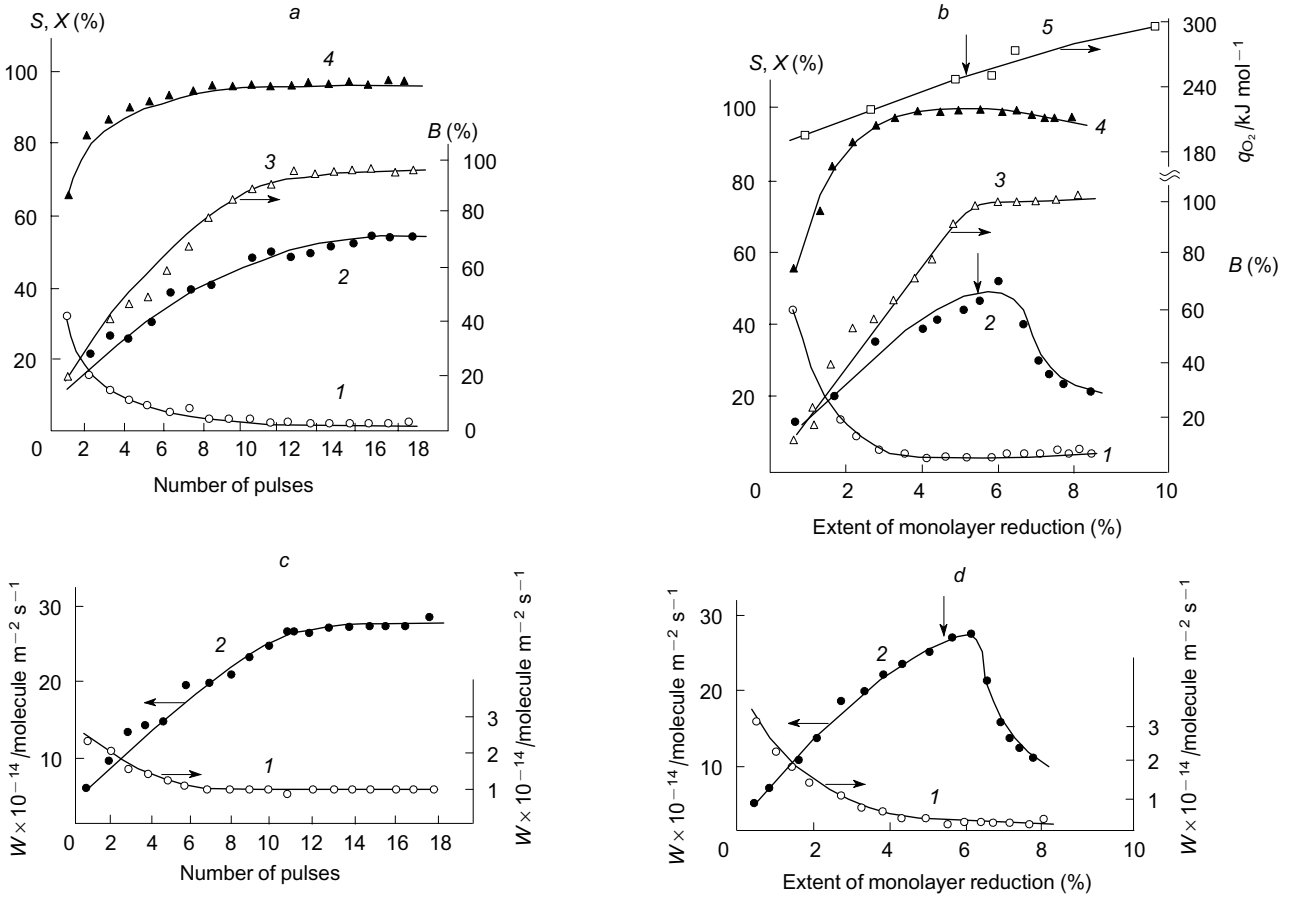


Figure 6. Changes in the catalytic properties of V–Mo oxide catalyst in the oxidation of acrolein (*a*, *c*) and reduction of catalyst (*b*, *d*). Adapted from Ref. 64.
(*a*, *b*): Selectivity to products of deep oxidation (*1*), acrolein conversion (*2*), carbon balance (*B*) (*3*), selectivity to acrylic acid (*4*), heat of adsorption of oxygen (q_{O_2}) (*5*); (*c*, *d*): rate of formation of products of deep oxidation (*1*) and rate of formation of acrylic acid (*2*).

isonicotinic acid, respectively.[38] According to G.K.Boreskov, 'to obtain products of partial oxidation, the binding energy of oxygen at a catalyst surface must be sufficiently low to provide the required rate of oxidation of the starting material, but at the same time high enough to ensure that further oxidation of the products of incomplete oxidation does not occur'.[21] 'Products of partial oxidation are formed and retained if the oxygen binding energy is higher than 250 kJ mol^{-1}'.[15] This condition is met by the highly selective V–Mo–M (M = P, Cs, Cu, Ti)[101] and V–Ti catalysts[32,33] containing strongly bound oxygen, *viz.*, the heats of adsorption of oxygen on the steady-state catalysts are 230–350 kJ mol^{-1} (Fig. 7). The heats of re-oxidation of the V–Ti and V–Zr oxide catalysts selective in the oxidation of methanol to formaldehyde also fall in this range, being equal to 240 and 245 kJ mol^{-1}, respectively.[63]

A classical method to establish the mechanism of oxygen involvement in the oxidation is to compare the rate of catalysis and the rate of reduction of the steady-state catalyst with the oxidizable reactant.

The rates of formation of products in the catalytic oxidation of acrolein on the V–Mo oxide catalyst[95] and formaldehyde on the V–Ti oxide catalyst[51] and the rates of catalyst reduction with acrolein and formaldehyde are listed in Table 3. For the V–Mo oxide catalyst, these rates are equal to each other. The rates of reduction of the steady-state Cu-, P-, Ti- and Cs- promoted V–Mo oxide catalysts with acrolein appeared to be equal to the rates of catalysis.[102] This points to realization of traditional Mars–Van Krevelen redox mechanism where the interaction of the oxidizable substance with the catalyst (reduction) and re-oxidation of the catalyst occur in different stages of the catalytic cycle.[17]

Catalysis on the V–Ti oxide catalyst occurs much faster than reduction. It follows that gaseous oxygen is involved in the concerted stage of re-oxidation of the catalyst and desorption of acid. This is a concerted (associative) mechanism according to Boreskov or the so-called modified redox mechanism according to modern terminology. This mechanism was for the first time reported in relation to the concerted stage of CO_2 desorption and catalyst re-oxidation in the oxidation of CO on Cr_2O_3 (Ref. 103) and ZnO (Ref. 104) and in deep oxidation of hexane[105] and butene[106] on ZnO and Cu_2O, respectively.

This mechanism of acid formation is realized in the oxidation of ethanol[34,35] and β-picoline on V–Ti oxide catalysts.[107] For the latter case, this was confirmed by comparing the IR spectra of the surface complexes of β-picoline in helium flow and in air flow.[107] Reactions in both media afford the same surface compounds that

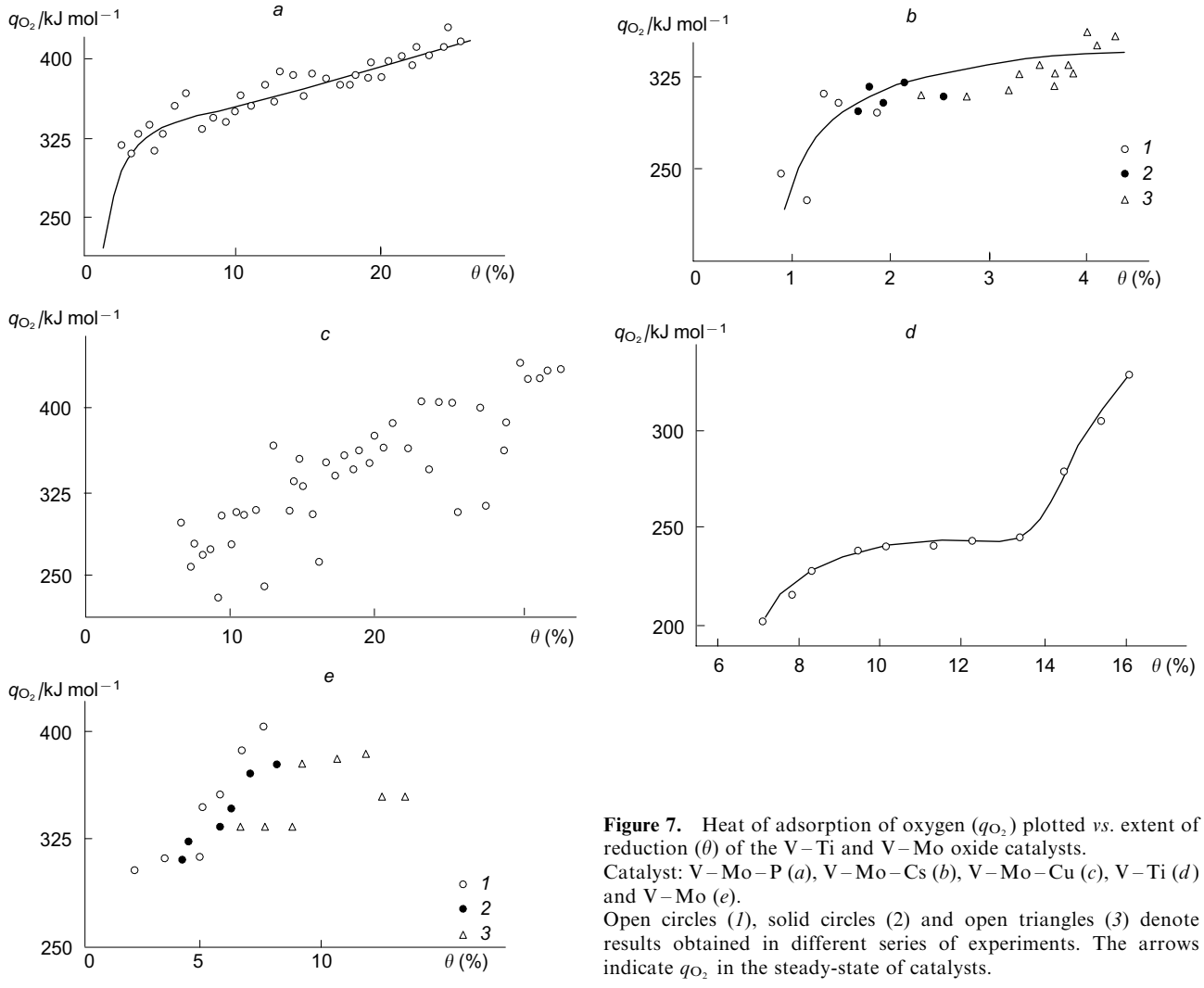


Figure 7. Heat of adsorption of oxygen (q_{O_2}) plotted *vs.* extent of reduction (θ) of the V–Ti and V–Mo oxide catalysts.
Catalyst: V–Mo–P (*a*), V–Mo–Cs (*b*), V–Mo–Cu (*c*), V–Ti (*d*) and V–Mo (*e*).
Open circles (*1*), solid circles (2) and open triangles (*3*) denote results obtained in different series of experiments. The arrows indicate q_{O_2} in the steady-state of catalysts.

Table 3. Rates of catalysis and rates of catalyst reduction with oxidizable reactant (for the steady state of the catalyst).

Catalyst	T/°C	Operating mode	x (%)	$W \times 10^{-15}$/molecule m^{-2} s^{-1}		S (%)		Ref.
				RCOOH [a]	CO_x	RCOOH [a]	CO_x	
			Reaction $C_3H_4O \longrightarrow C_3H_4O_2$					
V–Mo	180	Catalysis	6.0	0.68	0.01	98.0	2.0	95
	180	Reduction	5.8	0.60	0.01	98.0	2.0	95
	180	Catalysis	6.1	0.68	0.01	98.0	2.0	95
	260	"	31.8	0.84	0.04	95.3	4.7	95
	260	Reduction	23.2	0.74	0.03	96.0	4.0	95
	260	Catalysis	31.9	0.84	0.04	95.0	5.0	95
			Reaction HCHO $\longrightarrow$ HCOOH					
V–Ti	110	Catalysis	20.0	5.80	0.15	98.4	1.6	51
	110	Reduction	4.5	0.60	0.07	92.0	4.0 [b]	51
	110	Catalysis	20.0	5.70	0.14	98.0	2.0	51
	120	"	28.0	6.70	0.20	97. 0	3.0	51
	120	Reduction	8.0	1.30	0.10	93.0	4.0 [b]	51
	120	Catalysis	27.0	6.60	0.20	97.0	3.0	51

[a] Acrylic or formic acid. [b] Plus methyl formate to 100%.

undergo identical transformations. However, nicotinic acid is formed only in air as was confirmed by the appearance of the bands in the region of 1770–1700 cm^{-1} (Fig. 8).

The decomposition of acetate and formation of acetic acid (band at 1664 cm^{-1}) are also observed only in the oxygen-containing reaction mixtures (Fig. 9). In the absence of oxygen, the concentration of acetate ion (bands 1532 and 1444 cm^{-1}) in the reaction medium increases, reaches a maximum value at 200 °C (see Fig. 9 *b*) and then remains unchanged. In the oxygen-containing reaction

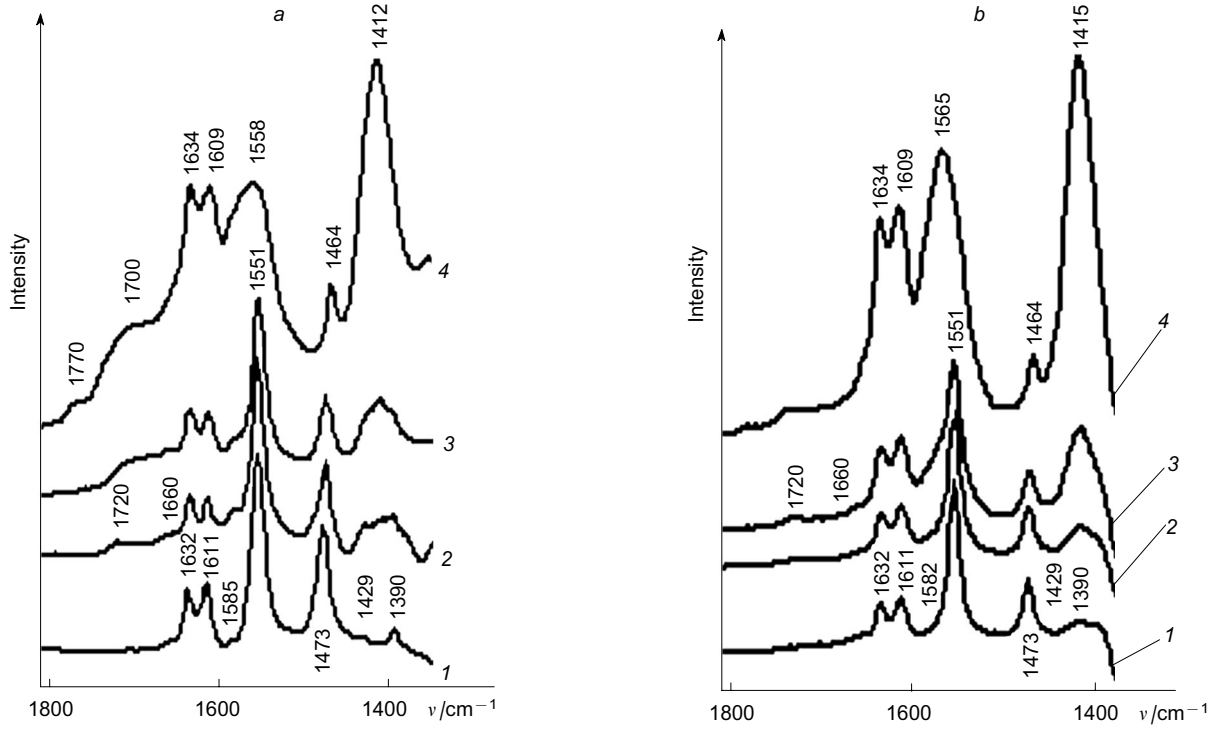


Figure 8. IR spectra of surface compounds formed in the oxidation of β-picoline on V–Ti oxide catalyst in air (*a*) and in helium atmosphere (*b*) at 120 (*1*), 180 (*2*), 200 (*3*) and 260 °C (*4*). Adapted from Ref. 107.

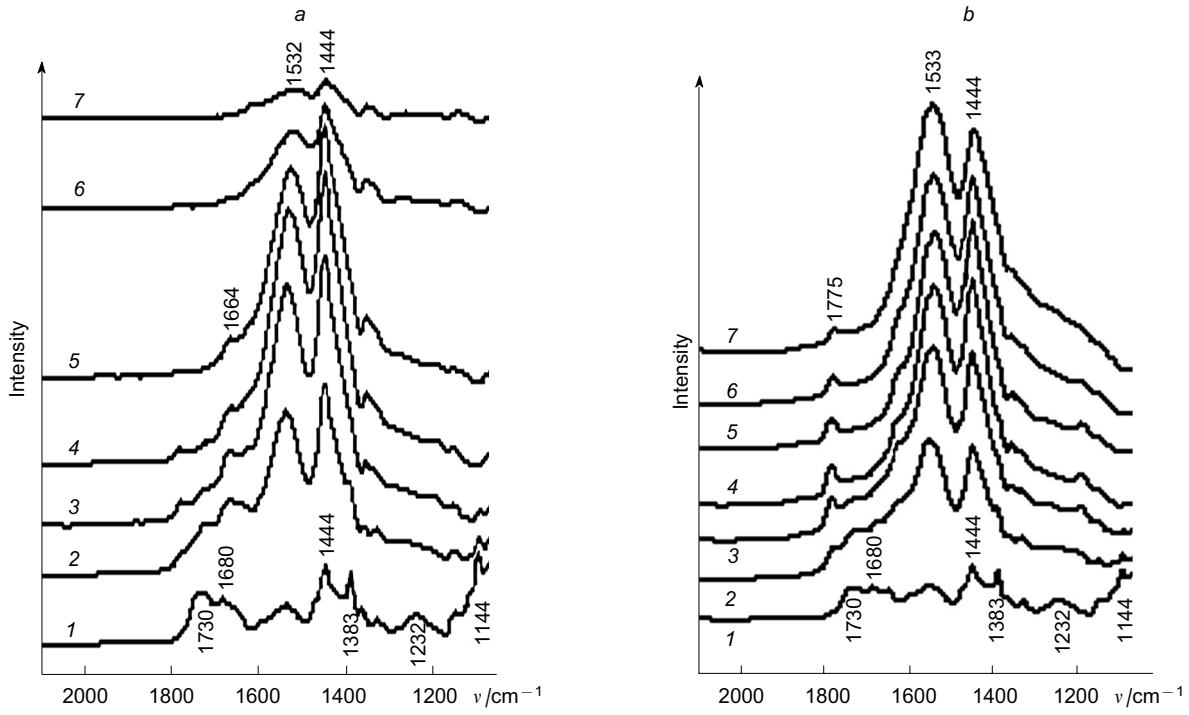


Figure 9. IR spectra of surface compounds formed in the oxidation of ethanol on V – Ti oxide catalyst in air (*a*) and in helium atmosphere (*b*) at temperature 100 (*1*), 130 (*2*), 150(*3*), 180 (*4*), 200 (*5*), 230 (*6*) and 250 °C (*7*). Adapted from Ref. 34.

medium the concentration of acetates also reaches a maximum value at 200 °C and then abruptly decreases with increasing temperature due to conversion of acetate ions to acetic acid, which occurs only in the oxygen-containing medium.

A distinctive feature of the most selective catalysts (V – Mo and V – Mo – Cu) is the high mobility of bulk oxygen (see Fig. 7). The oxygen mobility is not directly related to selectivity. The lower the binding energy of oxygen the higher the mobility of oxygen in same-type catalysts. High oxygen mobility provides a constant binding energy over a wide range of reduction extent under the reaction conditions, which leads to independence of selectivity on the composition of the reaction mixture.

Three versions of the Mars – Van Krevelen mechanism for oxidative dehydrogenation of propane were considered in a review.[108] Two of them describe a conventional mechanism and differ only in the type of the catalyst oxygen species participating in the reaction, namely, the catalyst lattice oxygen or superstoichiometric oxygen adsorbed from the gase phase onto reduced catalyst sites. In the third case, the desorption of products (propylene and water) and re-oxidation of catalyst occur at the same (joint) stage. Clearly, this mechanism is related to the modified redox mechanism described above.

The Mars – van Krevelen mechanism was proposed [109] for the oxidation of furfural to maleic anhydride on the V – Al oxide catalyst; here, re-oxidation of the reduced active site is the slow stage while selective oxidation requires a large excess oxygen with respect to the reactant.

The involvement of catalyst lattice oxygen in the formation of intermediate complexes was confirmed in many studies. In most cases, the reactions proceeded by the conventional Mars – van Krevelen mechanism.

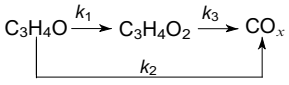
5. Influence of the bond strength of surface complexes on the direction of chemical reactions

Strong bonding of oxygen is a necessary but not sufficient condition for selective behaviour of the reaction. 'The specific interaction of an oxidizable substance with a catalyst plays a key role in reactions of selective oxidation. In this case, both a strong interaction of an oxidizable substance with the participation of weakly bound oxygen and a weak interaction with the participation of strongly bound oxygen on the catalyst surface are observed. In the former case, the desorption yields only the products of complete oxidation, in the latter case, the partial oxidation products are produced'.[15]

This can be illustrated by the data for two catalysts of acrolein oxidation listed in Table 4. As can be seen, both catalysts are characterized by close values of the heat of adsorption of oxygen but differ in selectivity.

The series-parallel scheme of acrolein oxidation on both catalysts (Scheme 2) is based on the results of kinetic data processing using the first-order equation with respect to the oxidizable substance and acid.

Scheme 2



$$S^0_a = \frac{k_1}{k_1 + k_2} \quad (2)$$

$$S^0_{CO_x} = \frac{k_2}{k_1 + k_2} \quad (3)$$

$$b = \frac{k_3}{k_1 + k_2} \quad (4)$$

Table 4. Catalytic and adsorption properties of catalysts in the oxidation of acrolein.

S_a^0 (%)	$S_{CO_x}^0$ (%)	b	Relative amount of adsorbed species (%)		q_{O_2} /kJ mol^{-1}
			C_3H_4O [a]	$C_3H_4O_2$ (see [a])	
Catalyst — $V_2O_4-9\,MoO_3/SiO_2$ (Refs 42 and 43)					
96	4	0.01	$\frac{98}{2}$	$\frac{98}{2}$	250
Catalyst — β-$CoMoO_4$ (Ref. 110)					
88	10	0.04	$\frac{93}{7}$	$\frac{86}{14}$	260

Note. Notations are as follows: S_a^0 is the selectivity to acid at zero conversion and $S_{CO_x}^0$ is the selectivity to carbon oxides at zero conversion: from this point on, the numbers in the rows in the formulas of the catalysts denote the mole fractions of the components.

[a] The numerator and the denominator indicate the relative amounts of the weakly (T_{des} = 70–350 °C) and strongly bound forms (T_{des} = 350–500 °C), respectively.

where k_1-k_3 are the rate constants for the corresponding stages.

Products of deep oxidation are formed from acrolein along with acrylic acid; these processes are characterized by the parameters $S_{CO_x}^0$ and S_a^0. Consecutive oxidation of the acid is characterized by the afteroxidation constant b.

The amounts of the strongly and weakly bound forms of acrolein and acrylic acid adsorbed on the V–Mo/SiO_2 (Refs 42 and 43) and β-$CoMoO_4$ catalysts [110] were obtained from temperature-programmed desorption measurements. The data in Table 4 demonstrate the effect of the strength of the adsorbed acrolein and the product of its oxidation, that is, acrylic acid, on the selectivity in the oxidation of acrolein. There is a clearly seen correlation between the ratio of the strongly (T_{des} = 350–500 °C) and weakly (T_{des} = 70–350 °C) bound forms of acrolein and the parameters $S_{CO_x}^0$ and S_a^0. The ratio of the strongly and weakly bound acid correlates with the afteroxidation constants b. For β-$CoMoO_4$, the ratio of the strongly and weakly bound forms of acrolein and acid and, therefore, the $S_{CO_x}^0$ and b values are larger than those for the V–Mo oxide catalyst. For the same reason, the selectivity S_a^0 is much lower. These results show that the strength of the surface compounds of the starting reactant and product is the key factor governing the direction of chemical reactions.[111]

The strength of surface compounds was evaluated from the heats of adsorption of acrolein and acrylic acid at the observation temperatures [112] determined for the binary V–Mo oxide catalyst and for V–Mo oxide catalysts promoted with copper, phosphorus, titanium, sodium, potassium and caesium. Promoting with these elements does not change the phase composition and structure of the active component, but has a strong effect on the acidity of the active site,[112] which leads to significant changes in the catalytic properties.[100] The acidity of the active site is a key parameter determining the strength of surface compounds of acrolein (weak base) and acrylic acid.

The strength of surface formates on the V–Ti oxide catalyst was evaluated from the heat of desorption of formic acid.[113] At real surface coverages by the bidentate formate under the reaction conditions specified in Ref. 114, the heat of desorption of formic acid was 70–80 kJ mol^{-1}.[113] This value coincides with that obtained from the density functional theory (DFT) calculations [115] and thus it is a quantitative measure of the bond strength of formates, which governs the selectivity of the formaldehyde oxidation.

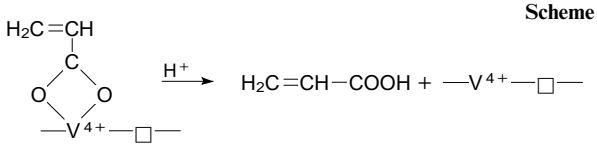
The adsorption and catalytic properties of the V–Mo and V–Ti oxide catalysts of different reactions are collected in Table 5. As can be seen, additives influence the strength of surface compounds and the binding energy of oxygen. The heat of adsorption of acid characterizes the energy of the bond between the carboxylate ion and the active surface site and serves a criterion determining further transformations or conservation of the product of selective oxidation. Doping with phosphorus increases the acidity of the active site and the strength of the adsorbed acrolein and causes S_a^0 to decrease and $S_{CO_x}^0$ to increase. Doping with alkali metals increases the basicity of the active sites and the strength of acrylate, accelerates the oxidation of acids but leaves S_a^0 untouched. Owing to high strength of carboxylate the direction of the reaction changes towards deep oxidation. For instance, as the heat of adsorption of acid on the V–Mo–Cs catalyst increases, the yield of the acid decreases due to increased afteroxidation (afteroxidation constant b increases). Clearly, the heats q_R, q_a and q_{O_2} equal to 84, 75 and 230 kJ mol^{-1}, respectively, characterize the optimum catalyst. These values were determined for the V–Mo–Cu catalyst that provides the maximum yield of acrylic acid.

Based on analysis of the energy characteristics and taking account of the similarity between the mechanisms, one can conclude that the heats q_a = 75 and q_{O_2} = 230 kJ mol^{-1} are universal parameters characteristic of the formation of acids from any organic compounds on the oxide catalysts.

Studies on the oxidation of organic compounds of different nature and composition to carboxylic acids confirmed G.K.Boreskov's concept of the chemical nature of catalysis and on the decisive influence of the binding energy of surface compounds of reactants (oxygen, oxidizable compounds and products) on the direction of chemical reaction.[21]

Figure 10 demonstrates a correlation between the experimentally observed concentrations of the active sites and those calculated using the equation for the key stage of the reaction, that is, the decomposition of acrylate which proceeds as shown in Scheme 3.

Scheme 3



□ is oxygen vacancy

Desorption of acid releases the reduced active site in the oxidation state V^{4+}. For the binary V–Mo catalyst, competing adsorption studies of acrolein and NO showed [45, 64] that acrylate is bound to the V^{4+} cation. The concentration of V^{4+} in the binary and promoted vanadium–molybdenum catalysts was determined by chemical titration [97] and from the IR spectra of adsorbed benzonitrile.[94]

Table 5. Adsorption and catalytic properties of V–M oxide catalysts.

Catalyst	Heats of adsorption /kJ mol^{-1}			S^0_a (%)	$S^0_{CO_x}$ (%)	$b \times 10^2$	Yield (%)
	q_R	q_a	q_{O_2}				
Oxidation of acrolein to acrylic acid							
$V_2O_4-9\,MoO_3/SiO_2$	84	75	250	96.5	3.5	1.1	91.8
$V_2O_4-9\,MoO_3-CuO/SiO_2$	84	75	230	98.3	1.7	0.5	97.0
$V_2O_4-9\,MoO_3-0.5\,TiO_2/SiO_2$	–	75	270	97.0	3.0	0.7	93.7
$V_2O_4-9\,MoO_3-0.06\,P_2O_5/SiO_2$	117	75	335	88.0	12.0	1.1	82.8
$V_2O_4-9\,MoO_3-0.2\,Cs_2O/SiO_2$	84	95	325	97.0	3.0	5.8	81.4
Oxidation of formaldehyde to formic acid							
$V_2O_5-TiO_2$	–	71	210–250	97.0	3.0	4.0	85.0
Oxidation of β-picoline to nicotinic acid							
$V_2O_5-TiO_2$	–	–	210–250	90.0	5.0	–	82.0

Note. Notations are as follows: q_R is the heat of adsorption of aldehyde, q_a is the heat of adsorption of acid and q_{O2} is the heat of adsorption of oxygen.

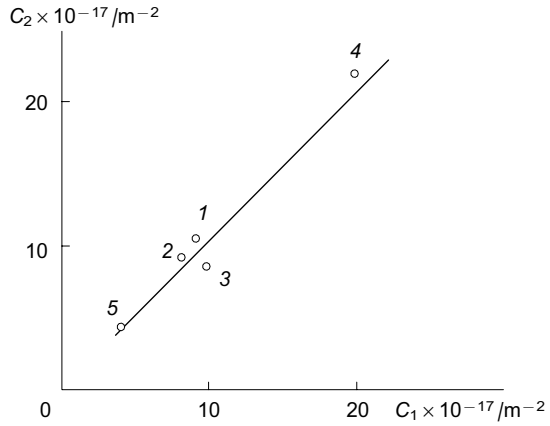


Figure 10. Correlation between the observed (C_1) and theoretical (C_2) concentrations of active sites (C_2 values were calculated using the equation for the key step of the reaction). Adapted from Ref. 94.
Catalyst: $V_2O_5-9\,MoO_3$ (*1*), $V_2O_5-9\,MoO_3-CuO$ (*2*), $V_2O_4-9\,MoO_5-0.5\,TiO_2$ (*3*), $V_2O_5-9\,MoO_3-0.06\,P_2O_5$ (*4*) and $V_2O_5-9\,MoO_3-0.2\,Cs_2O$ (*5*). Concentrations of active sites are given in the number of V^{4+} cations per m^2.

According to DFT calculations,[115] protonation occurs barrierlessly. The surface concentration of protons is much higher than that of acrylate; therefore, the equation for the rate of formation (W) of acrylic acid in the decomposition of acrylate does not include the concentration of protons and remains a first-order equation:

$$W = A \exp\left(-\frac{\alpha q_a + \beta q_{O_2}}{RT}\right)[V^{4+}] \quad (5)$$

where A, α and β are constants.

Since the surface compound, carboxylate, contains oxygen and the hydrocarbon residue of the acidic product, Eqn (5) includes the heats of adsorption of the acid and oxygen, measured for the steady-state catalysts.

Equation (5) is valid at α = 0.4 and β = 0.07. Confirming the importance of both components, it emphasizes the greater effect of the strength of the surface compound of the oxidizable reactant (α = 0.4) compared to oxygen (β = 0.07). Besides, the numerical values of these coefficients allow one to assess the acid–base (α) and redox (β) properties of catalysts. High selectivity of the V–Mo oxide catalysts is indicative of optimum combination of these properties.

In a generalized form the concept of selective oxidation developed by G.K.Boreskov can be described by a Brønsted–Polanyi type equation as the dependence of the activation energy (E) on the heats of adsorption (strength) of oxygen and oxidizable reactant

$$E = E_0 \pm \alpha q_i \pm \beta q_j \quad (6)$$

where q_i is the heat of adsorption of the oxidizable reactant in the form corresponding to the rate-limiting step of the reaction and q_j is the heat of adsorption of oxygen on the steady-state catalyst.

In accordance with the Brønsted–Polanyi equation, the plot of the rate of conversion of carboxylates *vs.* bond energy (q_a and q_{O_2}) has the shape of the so-called volcano curve (Fig. 11)[19,20] whose left branch corresponds to the rate-limiting step, *viz.*, the formation of carboxylate, while the right branch corresponds to the decomposition of the carboxylate. At $q_a = 0$, no carboxylate is formed, and the reaction is stopped at the preceding stage (formation of aldehyde or even product of dehydrogenation). The rate of formation of carboxylate increases as q_a increases up to the optimum value. If q_a exceeds the optimum value, the reaction rate decreases, while the strength of carboxylate increases; eventually, this leads to dead-end forms, namely, decomposition products and products of deep oxidation.

Clearly, the maximum in the volcano curve is reached at optimum q_a and q_{O_2} values. It corresponds to the highest rate of formation of acrylate and the highest selectivity to acid.

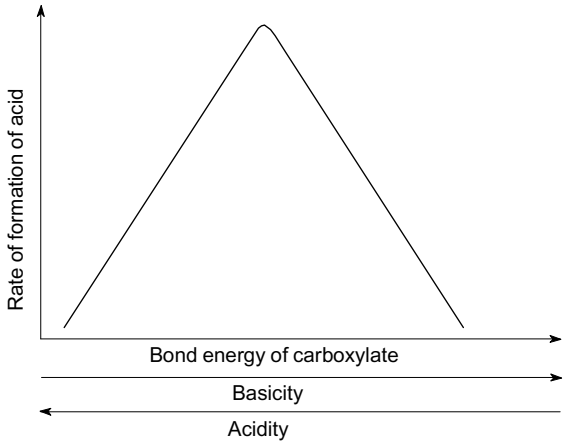


Figure 11. Volcano plot for the rate of formation of carboxylic acids as a function of the bond energy of carboxylates and the basicity and acidity of active sites.

6. Active sites of vanadium oxide catalysts of selective oxidation

'From the viewpoint of the foresight of the catalytic properties of oxides with respect to partial oxidation reactions the most important problem is to clarify the chemical nature of the centres for specific activation of oxidizable substances with the formation of intermediate compounds, that is, precursors of the partial oxidation products'.[16]

To date, the understanding of the 'nature of the centres for specific activation' is associated with the structure of the active component of catalysts.[59, 116, 117] Vanadium is a key element of many metal-oxide catalysts of selective gas-phase oxidation.[118] For instance, binary V–Mo catalysts and multicomponent V–Mo–Te and V–Mo–Te–Nb oxide catalysts based on them contain the orthorhombic and hexagonal phases (M1 and M2, respectively). The role of these phases in the oxidation and oxidative ammonolysis of propane and propylene, as well as in oxidative dehydrogenation of propane, ethane and ethanol is discussed in the literature.[65] Most researchers agree that the M1 phase is active and selective.[119–124] However, phase cooperation between M1 and M2 was also reported.[125, 126]

Considering the oxidation of acrolein on the V–Mo binary system, an X-ray amorphous phase VMo_3O_{11} with the characteristic reflections of the M1 phase ($2\theta = 22, 25^\circ$) was reported as active and selective.[127] More recently,[128, 129] amorphous and crystalline (trigonal, tetragonal and orthorhombic) phases of composition VMo_3O_n were synthesized. The activity of the phases in the oxidation of acrolein is as follows: orthorhombic > trigonal > amorphous > tetragonal. The selectivity of catalysts of the same chemical composition to acrylic acid is independent of their structure.

The trigonal phase exhibits the highest activity in the oxidative dehydrogenation of ethane.[130] In this case, the catalytic activity of the phases differs from that observed for the oxidation of acrolein, namely: trigonal > orthorhombic > amorphous > tetragonal. All structures were characterized by the same selectivity.

It was emphasized that the binary orthorhombic phase VMo_3O_n exhibits higher activity than the orthorhombic phase in the four-component V–Mo–Te–Nb system and, therefore, Te and Nb are not necessary additives. This is in agreement with our viewpoint, namely, the role of these elements is to stabilize the structure of the M1 phase.[131]

Vanadium species play the role of active sites for C–H bond activation in partial oxidation of organic compounds (ethane, propane, butane).[86, 132–138]

The reaction pathway for the conversion of propane into propylene on the V–Mo–Te–Nb catalyst was obtained from DFT calculations. Both V^{5+} and Mo^{6+} cations are involved in C–H bond activation in propane.[132–134] This conclusion was confirmed by the dependences of activity on the concentration of V^{5+} cations on the surface of the V–Mo–Te–Nb catalysts observed in the course of oxidative ammonolysis of propane [135] and oxidative dehydrogenation of ethane.[136] Havecker *et al.*[137] suggested that the M1 phase acts as support only, while the active sites for the oxidation of propane to acrylic acid consist of V^{5+} oxo species in close proximity to Te^{4+} sites embedded into a thin layer on the surface of the M1 phase.

In systems with the V–Te oxide catalyst, the V^{5+} cation is also involved in C–H bond activation in propane, while the Te^{6+}/Te^{4+} pair is responsible for C–H bond activation in the intermediate propylene and subsequent incorporation of oxygen into the allylic species.[138]

When butane is oxidized to maleic anhydride on the V–P catalyst, the V^{5+} cation also activates the C–H bond in the alkane and governs the catalyst activity.[86]

Supported vanadium oxide catalysts (in particular, vanadium–titanium ones) catalyze reduction of nitrogen oxides,[139] oxidation of benzene to maleic anhydride,[140] oxidation of *o*-xylene to phthalic anhydride,[141, 142] oxidation of methane to formaldehyde,[143, 144] oxidation of methanol to formaldehyde,[145] dimethoxymethane [146] and methyl formate,[147] as well as oxidation and ammoxidation of alkylpyridines [148, 149] and oxidative dehydrogenation of alkanes.[150, 151]

The focus of research into V–Ti oxide catalysts is the same as in the case of vanadium–molybdenum ones.[152–155] First of all, it involves structure determination of vanadium oxide species on the support surface. This was a subject of special issues of *Applied Catalysis A* [156] and *Catalysis Today* [157, 158] journals and a number of reviews (see, *e.g.*, Refs 40, 151, 159–161).

Numerous studies showed that the surface of vanadium oxide catalysts is covered with monomeric and polymeric (oligomeric) VO_x species and V_2O_5 crystallites. Their relative concentrations depend on the content of vanadium, the surface area and the type of support. In particular, only surface vanadium oxide species, either monomeric (isolated) or polymeric (oligomeric), are observed at low total concentrations of vanadium expressed as the number of V atoms per square nanometre. As the content of vanadium exceeds a value of about 8 vanadium atoms per square nanometre (for TiO_2, ZrO_2, Al_2O_3, CeO_2 and Nb_2O_5) or nearly 2.7 atoms per square nanometre (for SiO_2), bulk V_2O_5 phase appears in the catalysts.[162] Its amount increases with increasing vanadium concentration. For the V–Ti catalyst, a surface coverage of about 8 vanadium atoms per square nanometre is treated as monolayer coverage.[162]

The authors of most studies believe that monomeric and polymeric monolayer catalysts are more active than the V_2O_5 phase.[163–170] Different kinds of monolayer catalysts exhibit activity in different reactions. Polymeric VO_x species are active in oxidative dehydrogenation of butane to butylene and butadiene.[164] Monomeric VO_x species are active in oxidation of ethanol to acetaldehyde.[152, 165] According to

DFT calculations, conversion of methanol into formaldehyde occurs on two adjacent monomeric vanadium sites or one dimeric site.[166] The formation of formaldehyde from methanol on a dimeric site is thermodynamically more favourable than om monomeric sites.[167] Monomeric and polymeric VO_x species are more active than the V_2O_5 phase in the oxidation of toluene to benzaldehyde and benzoic acid.[168] It is believed that polymeric species are more active than monomeric ones in these reactions.[169] Monomeric VOx species are the most active in isopropanol conversion into acetone.[170]

It was shown that oligomeric VO_x species are most active in oxidation of ethanol to acetic acid,[35] oxidation of methanol to dimethoxymethane and methyl formate and oxidation of formaldehyde [171] to formic acid.[172] Monolayer species are also active in oxidation of β-picoline to nicotinic acid.[37]

Selective oxidation of formaldehyde, ethanol, acrolein and picolines has a common feature, *viz*., the carboxylate form of acid precursors (see Fig. 1–4) and reversibly adsorbed acids (see Fig. 5) bound to vanadium cations. Irrespective of the catalyst composition (multicomponent V–Mo–Te–Nb catalysts or vanadium oxide species on various supports) vanadium is the active carboxylate binding site. The strength of carboxylates is determined by the oxidation state of vanadium. Using competitive adsorption of acrolein and NO, it was established that acrylate is bound to the V^{4+} cation.[45,64] According to quantum chemical calculations,[48,115] the formate is bound to the V^{3+} cation. Binding of V^{3+} cations to formate [173] and acetate [34] was also established by *in situ* X-ray photoelectron spectroscopy.

Density functional theory calculations [115] of the energy profiles along the pathways of the formaldehyde oxidation on the V–Ti oxide catalyst showed that the strength of the bond between the formate and the catalyst surface depends on the oxidation state of vanadium. Formate is weakly bound to V^{5+} and its decomposition affords formic acid. The heat of acid desorption is 71 kJ mol^{-1}. The calculated heat of acid desorption upon decomposition of formate stabilized on V^{3+} is 135 kJ mol^{-1}. This formate is strongly bound to the active site and decomposes into carbon oxides in helium flow with increasing temperature. In oxygen-containing reaction mixture, vanadium is oxidized to V^{5+}, the energy of formate decreases and acid desorption becomes possible. Desorption of formic acid accompanies the decomposition of carboxylates at the joint stage involving re-oxidation of the catalyst by gaseous oxygen. This mechanism is also observed in the oxidation of 3-picoline and ethanol on the vanadium–titanium catalyst. It is called associative mechanism because acid is formed at the joint stage involving re-oxidation of the catalyst.

The associative mechanism is realized in the oxidation of *o*-xylene to phthalic anhydride [174] and in the oxidation of toluene to benzaldehyde [175] and to maleic anhydride.[176] Participation of molecular oxygen in the formation of products of selective oxidation is a distinctive feature of the V–Ti oxide catalysts. Oxidation of organic compounds involves multielectron transitions, and vanadium can be reduced to V^{3+} under the reaction conditions because the catalyst contains no other variable-valence elements (*e.g*., Mo^{6+}). We believe that it is high extent of reduction of the active sites that underlies realization of the associative mechanism on the V–Ti oxide catalysts.

In the oxidation of acrolein, vanadium can be reduced only to V^{4+} owing to close proximity to the highly charged Mo^{6+} cation. The Mo^{6+}/Mo^{5+} and V^{4+}/V^{3+} pairs have very close redox potentials; therefore, no deep reduction of vanadium occurs in the presence of molybdenum.

The basicity of V^{3+} cation is higher than that of V^{4+}, so carboxylate ions are more strongly bound to V^{3+}. Removal of carboxylate ions requires an additional energy which is supplied *via* participation of molecular oxygen in the associative mechanism at the joint stage involving decomposition of surface compounds and re-oxidation of the catalyst.

Carboxylates form weak bonds with both V^{5+} and V^{4+} ions, as demonstrated by the close values of the heats of adsorption of acrylic and formic acids equal to 75 (Ref. 113) and 71 kJ mol^{-1} (Ref. 112), respectively. Weak bonding of the starting reactant (heat of adsorption is 57 kJ mol^{-1}) as condition for selective transformation was reported for propane oxidation to acrylic acid on the V–Mo–Te–Nb catalyst activated in argon flow at 600 °C.[137]

The surface cations V^{5+} and V^{4+} exhibit weak acid properties and thus provide optimum bonding of carboxylates to the catalyst surface and, correspondingly, decomposition of these complexes under the catalysis conditions occurs without breakdown of the hydrocarbon skeleton. Likely, the heat of acid adsorption (desorption) of the order of 70–80 kJ mol^{-1} is a universal characteristic of selective oxidation of organic compounds to carboxylic acids.

The involvement of vanadium, as key element of complex oxide catalysts, in these reactions was also shown in some other studies.[177–179] The salt-like surface compound, *viz*., benzoate stabilized on the vanadium ion of the V–Sn oxide catalyst was for the first time observed by Sachtler *et al*.[177] in the formation of benzoic acid. Benzoate ions coordinated to vanadium cations are thought to be intermediates of formation of benzoic acid and oxidation of toluene.[178] It is believed that the reduced vanadium species (V^{4+}) is active in selective oxidation of butene to acetic acid.[179]

It is vanadium, a unique component of oxide catalysts of selective oxidation, that was considered by Golodets [180,181] as having optimum acid–base properties to form weakly bound salt-like compounds.

A concept of acid–base interactions between gaseous reactants and active sites of solid catalysts was developed by Stair.[182] The formation of the surface bond is treated as donor-acceptor interaction between Lewis acids (metal cations) and bases (oxygen) and reactants. Reactants with the lone electron pair on a certain atom (oxygen atom in aldehydes and alcohols and nitrogen atom in picolines) transfer the unpaired electrons to the acidic Lewis site, and the degree of electron transfer specifies the strength of the bond formed. Therefore, the strength of the bond between the reactant and the catalyst active site depends on the catalyst acidity. In accordance with Védrine and Fechete [10] and Takehira and co-workers,[71] the acidic surface favours desorption of acidic product of partial oxidation while the basic surface favours desorption of basic product of partial oxidation, thus reducing the selectivity to products of complete oxidation, namely, carbon oxides.

Introduction of promoters is an efficient tool for controlling the acid–base properties. Molybdenum and tungsten oxide additives increase the acidity of the V–Ti oxide catalysts, while gallium, lanthanum and zinc oxides decrease it.[183] The effect of promoters on the Lewis acidity

of the oxide catalysts and on the binding energy of the oxide catalyst oxygen was thoroughly analyzed in a review.[184] Additives can influence both the activity of catalysts by varying the structure and redox properties of the active component and the selectivity of catalysts by varying the acid–base properties and the forms of the catalyst oxygen species.[185]

There is considerable literature on the effect of additives on the acid–base and catalytic properties.[185–195]

Multicomponent promoting made it possible to design efficient catalysts of propane oxidation to acrylic acid[186] and of propane oxidative ammonolysis to acrylonitrile.[187] In the multistage conversion propane → propylene → acrolein → acid, vanadium is the active site of the formation of acrylic acid from intermediate aldehyde on the Mo–V–Te (Ref. 188) and Mo–V–Te–Nb oxide catalysts.[131] The acidity of the vanadium active site in the binary vanadium-molybdenum[189] and four-component Mo–V–Te–Nb catalysts[135,187] of propane ammoxidation is optimized by incorporating bismuth and calcium having higher basicities compared to the elements of the parent composition. A decrease in the acidity of the active sites upon adding Bi and Ca is accompanied by a decrease in the strength of basic surface compounds (aldehyde, nitrile), which enhances their desorption and increases the selectivity, especially at high conversions.[135,189,190] The yield of acrylic acid on the Mo–V–Te–Nb catalyst can be increased by promoting with phosphorus having high electronegativity, which increases the acidity of the active site.[193]

Among promoters of $CrVO_4$, which catalyzes the synthesis of nicotinic acid, the most efficient are small additives of phosphorus which seem to optimize the acidity of the active site.[72–75]

It is vanadium, as component of complex oxide catalysts of glycerol oxidation, that is the active site of conversion of intermediate acrolein into acrylic acid.[87,194] Phosphorus additives to the W–V–Nb catalyst increase the acidity of the vanadium site and the yield of the acid, as well as decrease consecutive oxidation of the acid into CO_x.

The acidity of the active site M–O–S of the monolayer MO_x species (M = Mo, V), which is determined by the electronegativity of the support (TiO_2, Al_2O_3) cations, is the key parameter of oxidative dehydrogenation of alkanes C_2–C_5. The high acidity of VO_x species predetermines higher selectivity compared to the MoOx species on the same supports.[195] The support also influences the forms of oxygen species. For instance, the support (ZrO_2 and TiO_2) changes the binding energy of oxygen in the VO_x species when carrying out oxidation of formaldehyde to formic acid on supported vanadia catalysts.[172]

Potassium additives decrease the acidity of surface vanadia and increase the selectivity in epoxidation of propylene.[191] Small potassium additives also increase the activity and selectivity of the vanadium-titanium catalyst in the oxidation of *o*-xylene to phthalic anhydride.[192]

The volcano curve shown in Fig. 11 characterizes the influence of the acid–base properties of the catalyst on the properties of carboxylate. An increase in basicity (decrease in acidity) up to the optimum value favours an increase in q_a and in the rate of formation of carboxylate [minus sign in Eqn (6), left branch]. An increase in basicity above the optimum value causes further increase in q_a, a decrease in the rate of carboxylate decomposition [plus sign in Eqn (6), right branch], an increase in the strength of carboxylate and eventually leads to decomposition of the carboxylate.

Summing up, irrespective of the phase and chemical composition and structure of catalysts, vanadium is the active site binding to the key intermediate. The oxidation state and acidity of vanadium govern the strength of surface complexes and the direction of reactions.

7. Conclusion

Materials presented in this review illustrate the chemical approach of Academician G.K.Boreskov to analysis of selective oxidation processes. His ideas appeared to be fruitful in this branch of the science of catalysis, and we tried to demonstrate them by considering heterogeneous selective oxidation of certain organic compounds to carboxylic acids. The essence of Boreskov's concept consists in the decisive influence of the structure and binding energy of surface intermediates on the direction of chemical reactions.

In oxidation of organic compounds of different nature and composition to carboxylic acids, surface carboxylates are the direct precursors of acids, and the decomposition of carboxylates is the key stage of formation of the target product. The correlation between the experimentally observed concentration of the active sites and that calculated using the equation for the rate-limiting step of the reaction, *viz.*, decomposition of acrylate, obtained in the studies of acrolein oxidation to acrylic acid characterizes the influence of the strength of the bonds formed by carboxylate and oxygen on the direction of the reaction. Selective course of the reaction is governed by the bond energy of carboxylate provided that strongly bound oxygen is present in the system under study. Strongly bound intermediates are converted to the decomposition and deep oxidation products while weakly bound intermediates are converted to acids. Activation of the oxidizable reactant is of no consequence for the deep oxidation processes, the activity is determined only by the strength of the bond formed by the catalyst oxygen.

The quantitative criteria for the binding energy of carboxylate (q_a) and oxygen (q_{O_2}) are determined. They govern selective course of the reaction. An optimum catalyst is characterized by $q_a = 75$ kJ mol^{-1} and $q_{O_2} = 230$ kJ mol^{-1}.

Unique combination of the acid–base and redox properties of vanadium favours the binding of carboxylates in a nearly optimum energy state.

In most cases oxidation of organic compounds on vanadium oxide catalysts proceeds by the two-stage Mars–Van Krevelen redox mechanism, according to which acrolein is oxidized to acrylic acid on the vanadium–molybdenum catalyst. The formation of carboxylic acids on vanadium–titanium catalysts proceeds by the modified redox or associative (or joint, following G.K.Boreskov) mechanism. The product of the reaction on these catalysts, that is, carboxylic acid, is released into the gas phase at the joint stage involving re-oxidation of the catalyst by gaseous oxygen. The difference between the mechanisms of the reactions on the vanadium–molybdenum and vanadium–titanium catalysts is due to different oxidation states of vanadium in the active sites, namely, V^{4+} in the former and V^{3+} in the latter case. Carboxylate weakly binds V^{4+} and can release into the gas phase without re-oxidation of the active sites. On the contrary, the

V^{3+} cation binds carboxylate strongly, and the release of acrylic acid requires compensation in the form of re-oxidation of the active sites by gaseous oxygen. Thus, ready desorption of the product is the key characteristic of the reaction mechanism.

The available numerical values of the bond energies of oxygen and acidic product can serve as criteria for the search of selective catalysts of oxidation of various organic compounds to carboxylic acids.

Various *in situ* spectroscopic methods (first of all, vibrational spectroscopy) provide a way to gain a better insight into specific features of the mechanisms of heterogeneous catalytic reactions on the molecular level. Revealing the details of the mechanism of a particular catalytic reaction on the molecular level will enable targeted optimization of the acid – base and redox properties of the catalyst active sites.

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