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Mechanism of heterogeneous oxidation of acrolein to acrylic acid

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ABSTRACT. A summary and analysis is given of results in the literature, and of our own results, of investigations into the mechanism of the heterogeneous oxidation of acrolein on oxide catalysts. The mechanism by which acrylic acid and oxides of carbon are formed from acrolein and oxygen is discussed. General principles for the interaction of acrolein with oxide catalysts are considered, and special attention is given to the nature of adsorption centres and the role of surface compounds of acrolein and acrylic acid, in the course of acrolein oxidation. On the basis of a proposed mechanism, some principles are formulated for the specific selection of catalysts for the selective oxidation of acrolein to acrylic acid.

The bibliography contains 74 references.

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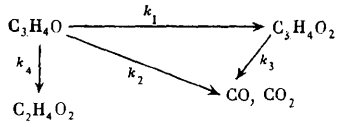
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I. Introduction

The selective oxidation of organic compounds constitutes a large area of heterogeneous catalysis. In a series of monographs and reviews, dedicated to the problem of selective oxidation of hydrocarbons,[1–7] consideration is given to the mechanism of reaction, the nature of catalytic action, and the chemical composition of catalysts. Special attention is given to activation of the oxidised substances and oxygen, the stages of reaction, and the state of the active surface. However, the question of the mechanism of selective conversion of unsaturated aldehydes, in particular acrolein, has received insufficient attention.

Heterogeneous catalytic oxidation of acrolein to acrylic acid is carried out abroad on the industrial scale—it is the second stage in the process for the synthesis of acrylic acid from propylene.[8–12] The practical value of this reaction has stimulated, especially in recent years, a large number of scientific investigations into the mechanism and kinetics of the conversion, and also the selection of catalysts. In the present work we have attempted to summarise the literature data, and also our own data, on the mechanism of the heterogeneous oxidation of acrolein and to reveal some principles for the course of this reaction.

For the oxidation of acrolein to acrylic acid, multi-component oxide catalysts are used. The reaction proceeds by a consecutive-parallel scheme:



The principal products are acrylic acid and the oxides of carbon but, with some catalysts, acetic acid is also obtained. The small number of products and the difference in their acid-base properties from those of the starting material, make this reaction a convenient model for application of the ideas of Boreskov, on the intermediate chemical interaction of the catalyst with components of the reaction mixture, to the selection of catalysts. According to these ideas,[1] the direction of conversion of the intermediate surface compounds (SC), which are formed by interaction of the catalyst with the reaction mixture, is determined by the structure and bond energy of the SC.

Investigation of the reaction mechanism, i.e. defining the forms and energetic characteristics of the SC, the elucidation of their chemical bonding with the catalyst, and their directions of conversion into reaction products, is the most reliable route to an understanding of the nature of the catalytic action and to elaboration of the principles of catalyst selection. It is from precisely these points of view that we consider the available data for acrolein oxidation in the present work.

II. Mechanism by which oxygen takes part in the formation of acrylic acid and products of more deep-seated oxidation

Two mechanisms can be distinguished for the introduction of oxygen into the molecule which is undergoing oxidation: a step-wise mechanism, involving alternating oxidation and reduction of the catalyst by oxygen and the substances undergoing oxidation (the so-called oxidation-reduction mechanism) and a unified (associative) mechanism, with oxygen taking part in the gas phase.[13–16]

At the present time, for many selective conversion reactions of hydrocarbons, the oxidation-reduction mechanism for the participation of oxygen is well established.[17–20]

The question of whether one or other mechanism is in operation is determined by a direct comparison of the independently measured rates of catalysis and of catalyst reduction (or reoxidation), which are found in the stationary state. Equality of these rates indicates

the step-wise oxidation-reduction mechanism, but if the rate of catalysis exceeds the rate of reduction, participation by oxygen in the gas phase is indicated. It should be particularly emphasised that it is important to maintain the stationary state of the catalyst during the process of measurement, since it differs considerably from the initial state and depends on the composition of the reaction mixture.[21] With movement towards the stationary state, there are changes in the oxygen content and in the energy of its bonds with the catalyst, the oxidation state of the cations, and the concentration of the strongly-sorbed form of the substance being oxidised, all of which control change in the rates of the particular reactions and accordingly their selectivity. Hence, it follows that the extent of reduction should not change significantly during measurement of the rate of reduction for the stationary catalyst. If these conditions are not observed the rate of catalysis may exceed the rate of reduction, to an extent that increases as the heterogeneity of oxygen in the catalyst increases.

The overall situation is illustrated graphically in Fig. 1,[22,23] from which it can be seen that the stationary state (the plateau on all curves, Fig. 1*a*), differs considerably from the initial state with respect both to activity and selectivity. Comparison of Fig. 1, which shows movement of the catalyst towards the stationary state in the reaction mixture (0.2% C_3H_4O, 0.4% O_2, the remainder He), with Fig. 1*b*, which shows the changes observed in the reducing mixture (0.2%, 99.8% He), leads to the conclusion that the catalyst is reduced by the reaction mixture with the formation of strongly-bonded surface compounds. The latter follows from the absence of a carbon balance for the first pulses. Fig. 1*b* also indicates that even a few percent increase or decrease in the extent of reduction of the surface of the catalyst causes a sharp change in the rate of formation of acrylic acid and oxides of carbon. This picture is typical of catalysts for the oxidation of acrolein.[21] It is therefore necessary to maintain a constant surface composition of the catalyst during measurement of the rates of catalysis and reduction.

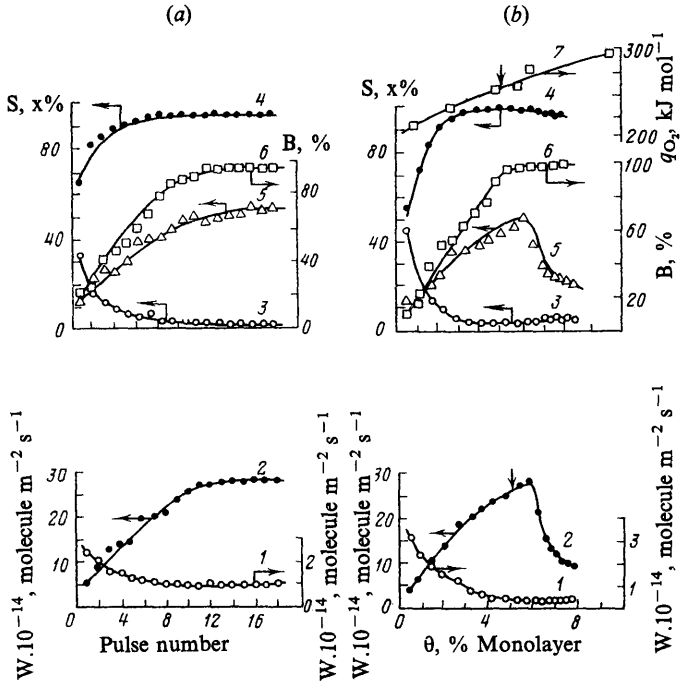


Figure 1. Dependence of the rate of formation of products of deep-seated oxidation (*1*), rate of formation of acrylic acid (*2*), selectivity for CO + CO_2 (*3*) and for $C_3H_4O_2$ (*4*), the extent of conversion of acrolein (*5*) and the carbon balance (*6*) on the impulse number of the reaction mixture (*a*) and on the extent of reduction of the surface (*b*); *7*, heat of adsorption of oxygen. Catalyst $V_2O_5.MoO_3/SiO_2$, T_r = 260 °C. Vertical arrows on Fig. 1*b* indicate the stationary state of reduction.

Table 1. Catalytic properties of vanadium- and cobalt–molybdenum catalysts for the oxidation of acrolein under the conditions of catalysis (mixture of C_3H_4O, 0.1%; O_2, 0.2%; He, 99.7%) and reduction (C_3H_4O, 0.1%; He, 99.9%).[21–24]

Catalyst *	*T*, °C	Working conditions	Conversion %	Reaction rate W.10^{-14} molecule m^{-2} s		Selectivity (%) for		Heat of adsorption O_2 kJ mol^{-1}
				C_3H_4O	$CO+CO_2$	C_3H_4O	$CO+CO_2$	
$V_2O_4 \cdot 9MoO_3/SiO_2$ **	260	Catalysis	54.0	29.0	1.07	96.5	3.5	255
		Reduction	48.0	27.0	0.60	97.8	2.2	
		Oxidation	–	–	0.40	–	–	
$V_2O_4 \cdot 9MoO_3/SiO_2$ **	300	Catalysis	49.1	12.5	1.50	89.3	10.7	247
		Reduction	48.5	11.8	1.20	91.0	9.5	
$V_2O_4 \cdot 9MoO_3 \cdot 1CuO/SiO_2$	300	Catalysis	58.1	14.1	1.20	92.1	7.9	226
		Reduction	56.5	14.5	1.20	93.6	7.4	
$V_2O_4 \cdot 9MoO_3 \cdot 0{,}2Cs_2O/SiO_2$	300	Catalysis	24.4	1.10	0.12	89.8	10.2	326
		Reduction	22.2	1.10	0.10	91.3	8.7	
$V_2O_4 \cdot 9MoO_3 \cdot 0{,}06P_2O_5/SiO_2$	300	Catalysis	22.4	8.20	1.58	83.5	16.5	335
		Reduction	19.8	7.30	1.10	86.6	14.3	
β-$CoMoO_4$	260	Catalysis	55.0	11.0	2.5	75.5	17.1	259
		Reduction	44.5	9.5	2.0	76.5	16.0	
		Oxidation	55.0	10.8	2.4	75.5	16.6	
α-$CoMoO_4$	260	Catalysis	44.5	0.98	6.05	11.8	73.5	259
		Reduction	36.0	0.87	4.80	9.4	68.0	
		Oxidation	—	–	2.00	–	–	

*Methods and conditions for the preparation of catalysts and their physico-chemical characteristics are described in Ref. 21.
**Samples obtained by different methods and differing in disperison.

Table 1 gives the rates of formation of acrylic acid and products of more deep-seated oxidation on vanadium- and cobalt-molybdenum catalysts.[21–24] As can be seen from Table 1, the rates of formation of acrylic acid for catalysis and reduction are close, indicating the oxidation-reduction mechanism for its formation. In the formation of products of more deep-seated oxidation, oxygen of the catalyst also participates; there is, however, a definite contribution by oxygen in the gas phase, as indicated in some cases by an appreciably higher rate of catalysis than the rate of reduction and the formation in the oxidising pulses of CO and CO_2. An analogous correlation of the rates of catalysis and reduction is also observed at other temperatures.

Table 2. Catalytic properties of tin–molybdenum catalysts for the oxidation of acrolein under conditions of catalysis and reduction.[27]

Catalyst	Working conditions	Contact time, s	Conversion %	Selectivity (%) for		
				$C_3H_4O_2$	$CO+CO_2$	Decomposition products
SnMoBiVO	Catalysis	0.54	34.2	5.0	95.0	0.0
	Reduction	0.54	32.2	5.3	94.4	0.7
	Catalysis	1.07	64.4	3.3	96.7	0.0
	Reduction	1.07	52.5	3.8	96.1	0.1
SnMoBiFeO	Catalysis	1.07	34.5	7.9	91.4	0.7
	Reduction	1.07	34.5	8.1	91.9	0.0
	Catalysis	0.54	30.5	12.8	86.2	1.0
	Reduction	0.54	31.0	11.3	88.0	0.7
SnMoBiFeNiO	Catalysis	0.54	18.6	14.0	84.2	1.8
	Reduction	0.54	17.4	18.2	81.8	0.0
	Catalysis	1.07	28.2	13.5	86.8	0.3
	Reduction	1.07	25.4	12.1	87.2	0.7

The oxidation-reduction mechanism for the formation of acrylic acid on a vanadium–molybdenum catalyst has also been confirmed by the relaxation method.[25] The oxidation-reduction mechanism for the formation of acrylic acid and the associative mechanism for the formation of CO and CO_2, were shown to occur on vanadium–molybdenum oxide catalysts, promoted by Na, Mn, Zn, and Cu.[26] This conclusion was drawn on the basis of kinetic data, which indicated that oxygen has different effects on the mild and deep-seated oxidation of acrolein and on the basis of the change in catalytic properties of samples by treatment of them with reaction mixtures with different oxygen contents.

An analogous conclusion that acrylic acid is formed exclusively by the oxidation-reduction mechanism, and that CO and CO_2 are formed primarily by the oxidation-reduction mechanism, follows from a comparison of conversion and selectivity under the conditions of catalysis and reduction, on promoted tin–molybdenum catalysts (Table 2).[27]

In the opinion of Yakubovich,[28] a step-wise oxidation-reduction mechanism is involved in the formation of acrylic acid and products of deep-seated oxidation, on molybdates of Cr, Cd, Ni, Ba, Co, Mn, Mg, Cu, Zn, Fe, and Ca.

The step-wise oxidation-reduction mechanism can therefore be considered to be established for the preparation of acrylic acid on catalysts of various composition. Products of deep-seated oxidation may be formed by the oxidation-reduction mechanism, with varying contributions from the associative mechanism.

The oxidation-reduction mechanism assumes that oxygen of the latice, generally considered[29–32] to be in the charged state, O^{2-}, takes part in the catalysis. Participation of lattice oxygen in the formation of acrylic acid and the oxides of carbon was demonstrated by isotopic labelling with ^{18}O in reduction experiments with acrolein and phosphomolybdic heteropoly acid.[33] The same is shown by other data.[34] On exposure of $K_3PMo_{12}O_{40}$ to acrolein vapour at catalyst temperatures of 150–300 °C, an ESR signal was observed, as a result of reduction to give an oxygen-deficient Keggin unit, with the gain of two electrons. From the IR spectrum it was established that the oxygen lost was a bridging oxygen atom (Mo–O–Mo). The same view that bridging oxygen participates in the formation of acrylic acid from acrolein, is held by other authors.[33]

It should be noted that the role of bridging or doubly bonded oxygen in the oxidative conversion of acrolein is scarcely discussed in the literature. But in the series of molybdates of elements of group II and period 4, it is those which contain molybdenyl bonds that are chosen.[28,35] The lowest selectivity for acrylic acid is observed for the molybdates of Ba, Ca, and Cd, which are exactly those for which molybdenyl doubly bonded oxygen (Mo=O) is absent.

In connection with the course of reaction by the oxidation-reduction mechanism and the participation of oxygen in the stage at which acrylic acid and products of deep-seated oxidation are formed, a question arises concerning the effect of the bond energy of oxygen to the catalyst on the direction of acrolein conversion and the rates of particular reactions.

For reaction by the two-stage oxidation-reduction scheme, a plot of the dependence of rate on the oxygen-catalyst bond energy shows a maximum, corresponding to optimum bond energy.[36] The ascending part of the curve corresponds to the case when reaction is limited to oxidation on the surface, and the descending part when its rate is determined by the loss of oxygen. A quantitative dependence of activity on bond energy has been found for a series of oxide catalysts in the oxidation of hydrogen, nitrous oxide, and ammonia, and also for the deep-seated oxidation of some hydrocarbons.[37] For all these reactions, the dependence of rate on the bond energy of oxygen with the catalyst follows a descending curve, i.e. the activity of the catalyst is lower, the higher the energy of its bonds with oxygen.

For complex reactions which include a series of parallel and consecutive stages, for each of which there is an optimum strength for the metal–oxygen bond (M–O), its influence on the activity of the catalyst, and especially on its selectivity, is not obvious.

Boreskov[38] has formulated the general requirements for catalyst selectivity: "The energy of the bond between oxygen and the surface of the catalyst must be sufficiently low to provide the required rate of oxidation of the starting material, but at the same time be sufficiently high to ensure that further oxidation of the useful products of incomplete oxidation does not occur".

This position is convincingly confirmed by the way in which selectivity depends on the extent of reduction of the surface, as found for many oxide catalysts in partial oxidation reactions of hydrocarbons.[21,39] Thus, for each catalyst, the selectivity for mild oxidation products invariably increases with the extent of oxygen removal but for products of deep-seated oxidation the selectivity falls. Also, since oxygen as a rule is not homogeneous on the catalysts investigated and its bond energy with the surface increases as a result of reduction, it is generally recognised at the present time that the absence of weakly-bonded oxygen is a requirement for

selectivity. In the oxidation of acrolein, the dependence of selectivity on the extent of reduction for each catalyst is analogous to that described for hydrocarbons and the same rule is applicable, requiring the absence of weakly-bonded oxygen for the course of reaction to be selective. However, the search for a correlation of selectivity and activity, with the bond energy of oxygen in a series of oxide catalysts, has led to complex and even contradictory results. Thus for simple oxides, the rate of formation of acrylic acid and products of deep-seated oxidation was seen to depend on the bond energy with oxygen (Fig. 2), but selectivity was not dependent on this parameter.[40] In contrast, it is established[28,35] that the energy of the M–O bond in a series of molybdates of Mg, Ni, Zn, Mn, Fe, Cr, Cu determines the selectivity precisely and does not influence activity. It should be noted that in the latter case the bond energy of oxygen was determined from the initial rate of reduction by samples of hydrogen. This rate undoubtedly characterises the initial state of the catalyst but since, as shown above, this differs considerably from the stationary state, it is doubtful whether the conclusions of the authors[28,35] can be considered to be sound.

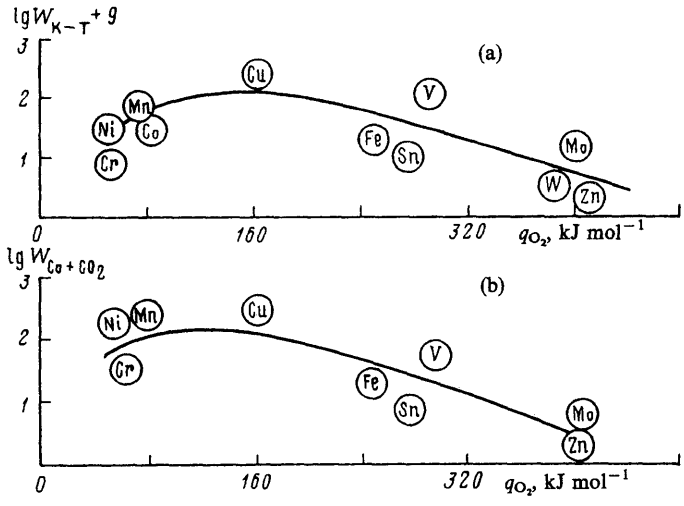


Figure 2. Dependence of the rate of oxidation of acrolein to the acid (*a*) and to Co + CO_2 (*b*) at 300 °C, on the bond energy of oxygen with the surface of oxide catalysts.[40]

An attempt has been made[28,35,40] to find a dependence of catalytic properties on the electronegativities of the cations, which determine the acidity of the catalyst. In the case of molybdates, the acidity of the catalyst does not influence selectivity but it affects the activation energy of the reaction.[28,35] For simple oxides, on the other hand, the selectivity depends on electronegativity.[40]

It is also very difficult to find any correlation of activity and selectivity with the bond energy of oxygen in the cases of V–Mo- and Co–Mo-catalysts. For these examples, as a measure of the bond energy, the heats of the adsorption (q) on the catalysts were determined in the stationary state, either by adsorption of oxygen on the previously reduced surface,[23,24,41] or *in situ*.[42]

As seen from Table 1, for the series of binary and promoted V–Mo-catalysts, only a fall in the rate of acrylic acid formation can be seen to occur with increase in the oxygen bond energy, whereas for the α- and β-modifications of $CoMoO_4$, which have identical values for the oxygen bond energy, the rates differ considerably. All catalysts in the stationary state are characterised by the presence of strongly-bonded oxygen (q_{O_2} = 225–335 kJ mol^{-1}) and with the exception of α-$CoMoO_4$ show high selectivity, but no quantitative correlation of selectivity with q_{O_2} is found.

The oxygen bond energy thus plays an important role in the oxidation of acrolein to acrylic acid but it is not possible to show a dependence of catalytic properties on q_{O_2} as the only parameter. In the oxidation of acrolein, and with the aim of selective oxidation,[36,38,43] it is therefore necessary to take account of other important factors, i.e. specific interaction of the substance being oxidised and the product of reaction with the catalyst surface.

III. Surface complexes of acrolein and acrylic acid and their role in the formation of reaction products

At the present time, basic information on the structure of surface compounds (SC) is obtained by the method of IR spectroscopy. Thermal desorption measurement has previously been widely used to provide evidence of the involvement of SC in the formation of reaction products but in recent years the use of spectroscopic methods *in situ*[44] has also made it possible to study the kinetics of conversion of the SC, and to measure the rate of the catalytic reaction simultaneously.

In Table 3, a summary is given of literature data on the structures of surface compounds of acrolein. Table 4 contains information on the catalysts on which these SC have been observed, together with their catalytic properties in the reaction of acrolein oxidation.

We have attempted on the basis of the literature data to reveal some general principles for the interaction of acrolein with oxide catalysts, giving special attention to the nature of the centre of adsorption and the role of surface complexes in the oxidation of acrolein. We do not dwell on the spectroscopic identification of SC, since this question is considered in detail elsewhere.[58,59]

Centres of adsorption on the surface of oxide catalysts may be protons, H^+ (Brønsted acid centres, BAC), coordinatively-unsaturated cations of transition metals (Lewis acid centres, LAC), and oxygen. These probably give rise to the diversity of the adsorbed forms of acrolein on the surface of oxide catalysts.

The presence of BAC on the catalyst surface, in the form of OH groups or delocalised protons, H^+, leads to the formation of a H-bonded complex with acrolein [SC (I), Table 3]. As a rule, this complex is weakly bonded with the surface and easily decomposes at room temperature as a result of brief pumping, or purging with helium, with the release of acrolein into the gas phase. It is therefore thought that hydrogen-bonded acrolein is not an intermediate in the process by which oxidation products are formed. However, in the presence of strong BAC, more strongly bonded SC (I) may be formed, which are able to participate in the reaction, and this also possibly occurs in the case of heteropoly acids (HPA) and heteropoly salts (HPS).[53]

The interaction of acrolein with aprotic centres (LAC) is accompanied by the formation of a coordinatively-bonded π-complex of acrolein (II), a surface acrylate (IV) and a carbonato-carboxylate complex (V). A number of workers have also observed the

formation of a σ-complex of acrolein (VI) at aprotic centres.[51,55] Surface ions of oxygen, O^{2-}, may also act as centres of adsorption, at which carbonyl-bonded acrolein (III) is stablised (Table 3).

Table 3. Surface complexes of acrolein.

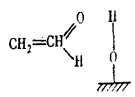
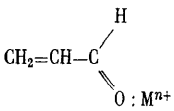
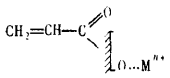
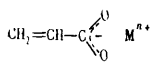
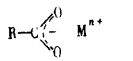
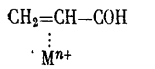
Structure	Name	IR absorption bands cm^{-1}	References
	Hydrogen-bonded acrolein	ν_{O-H} =3500 $\nu_{C=O}$ =1690–1705 $\nu_{C=C}$ =1625 δ_{C-H} =1370	[45–47]
	Coordinatively-bonded acrolein (II)	$\nu_{C=O}$ =1660–1690 $\nu_{C=C}$ =1625 δ_{C-H} =1370	[47–52]
	Carbonyl-bonded acrolein (III)	$\nu_{C=O}$ =1710–1730 $\nu_{C=C}$ =1625	[47–51, 53]
	Acrylate (IV)	$\nu_{as\,COO^-}$ =1520–1560 $\nu_{s\,COO^-}$ =1420–1460 $\nu_{C=C}$ =1640 δ_{C-H} =1370	[47–51, 54–57]
	Carbonato-carboxylate (V)	$\nu_{as\,COO^-}$ =1530 $\nu_{s\,COO^-}$ =1360	[50, 52]
	π-complex (VI)	$\nu_{C=C}$ =1490–1520	[51, 55]

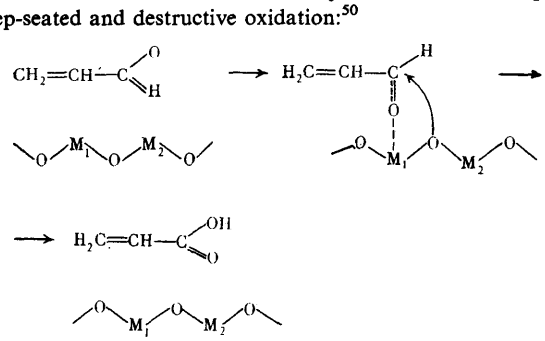
Table 4. Forms of adsorption of acrolein on oxide catalysts.

Chemical composition of the catalyst	Observed SC	Oxidation products	References
MoO_3/SiO_2	(II)	CO, CO_2, $C_3H_4O_2$	[52, 57]
Co–Mo=1 : 2	(II)	$C_3H_4O_2$, CO, CO_2	
Co–Mo + 2% MoO_3	(II)	$C_3H_4O_2$, CO, CO_2	[48, 50]
Co–Mo + 2% Co_3O_4	(II)	CO, CO_2	[48, 50]
Co–Mo + 7% V_2O_5	(II)	CO, CO_2	[48, 50]
Co–Mo + 10% V_2O_5	(II)	$C_3H_4O_2$, CO, CO_2	[49]
Co–Mo + 80% V_2O_5	(II)	$C_3H_4O_2$, CO, CO_2	[49]
V–Mo/SiO_2	(I) (II) (III) (IV)	$C_3H_4O_2$, CO, CO_2	[58]
V-Mo (solid solution of V in MoO_3)	(II) (III) (V)	$C_3H_4O_2$, CO, CO_2	[49]
Cr–Mo	(IV)	$C_3H_4O_2$, CO, CO_2	[54]
Cr–Mo–Te	(IV)		
Bi–Mo/SiO_2	(I)	–	[46]
SiO_2	(I)	–	[45]
MgO	(IV)	CO, CO_2, C_2H_4O $C_2H_4O_2$	[24, 56]
CuO	(V)	CO, CO_2	[24, 57]
Co–Mo/MgO	(II) (III) (IV) (VI)	–	[51]
Cr_2O_3	(V)	CO, CO_2	[52]
ZnO	(V)	CO, CO_2	[54]
$K_3PMo_{12}O_{40}$	(III)	$C_3H_4O_2$, CO, CO_2	[53]

*For name of the corresponding SC see Table 3.

As seen from Table 4, it is very difficult to link any form of surface complex directly with the defined chemical composition of the catalyst and with its catalytic properties: one and the same SC, for example coordinatively-bonded acrolein or acrylate, may be observed on a catalyst for the selective, deep-seated, or destructive oxidation of acrolein. Furthermore, on some catalysts, in spite of the rather diverse composition of the products of oxidation, only one surface complex was identified.

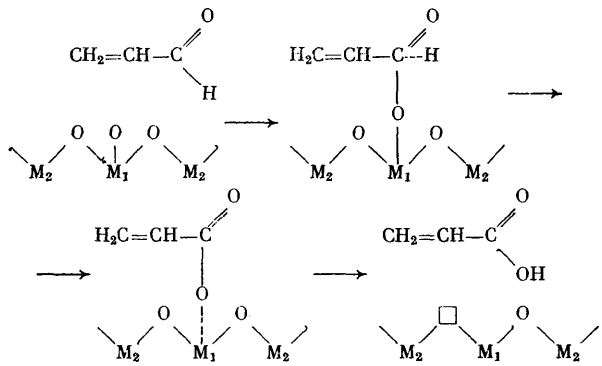
There are various opinions on the role of SC in the course of reaction. Thus, it is assumed that coordinatively-bonded acrolein is an intermediate in the formation of acrylic acid and also of products of deep-seated and destructive oxidation:[50]



where M_1 = $Mo^{6+}(T_d)$, $Mo^{5+}(T_d)$; M_2 = $Mo^{6+}(O_h)$, $Co^{2+}(O_h)$. The initial interaction presumably occurs with Mo^{6+} in either tetrahedral (T_d) or octahedral (O_h) coordination, or with Mo^{5+}.

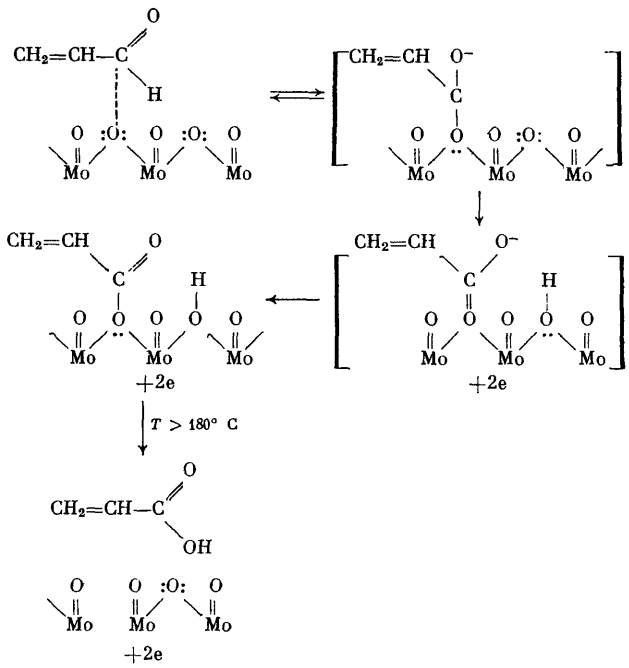
Coordinatively-bonded acrolein, for which the centres of adsorption on Co–Mo–V-oxide catalysts are Co^{2+} or Co^{3+} ions, in octahedral coordination, is thought[50] to be an intermediate in the formation of products of destructive oxidation. Certain authors believe[48–50] that surface acrylates [SC (IV)] are blind-alley forms for the adsorption of acrolein on Mo-containing oxide catalysts, whereas others[54] recognise acrylates as intermediate compounds both in the partial and the deep-seated oxidation of acrolein. The literature data allow a more definite judgement to be made on the direction of conversion for carbonyl-bonded acrolein (III) and surface carboxylates (V): almost all authors hold the opinion that (III) is an intermediate SC in the formation of acrylic acid, but (V) in the formation of deep-seated oxidation products.

The mechanism for the formation of acrylic acid through carbonyl-bonded acrolein is presented in the following scheme:[50]



$M_1=V^{5+}$, Mo^{6+} (*Oh*); $M_2=V^{4+}$

An analogous mechanism is also proposed for the oxidation of acrolein on phosphomolybdic heteropoly acids (HPA):[53]



This mechanism is confirmed by the results of an investigation into the adsorption of acrolein on $K_3PMo_{12}O_{40}$ by the methods of IR spectroscopy and ESR *in situ*.[53]

Another mechanism has been proposed[33] for the oxidation of acrolein and methacrolein on HPA, similar to the mechanism for the oxidation of aldehydes by chromic acid or permangante in solution.

The scatter of opinions on the mechanism of acrylic acid formation is due, first of all, to the use in most cases of insufficiently selective catalysts, with the result that several reaction products are obtained. Furthermore, the forms of adsorption were investigated under the conditions of pre-catalysis, when it is impossible to make a direct comparison between the rate for decomposition of the SC and the formation of reaction products. Such a comparison provides the most convincing evidence of the participation of one or other SC in the formation of reaction products.[60]

These conditions were observed in a study of the mechanism of acrolein oxidation by the method of IR spectroscopy *in situ* on a V–Mo–Si-oxide catalyst.[61,62] This catalyst possesses high selectivity: for acrolein conversions of less than 20%, acrylic acid is virtually the only reaction product, and with high conversions, further oxidation is also insignificant. Furthermore, good IR transmission of the sample made it possible to investigate the decomposition of surface compounds in the temperature range 25–350 °C, under the conditions of catalysis. Adsorption of acrolein on this catalyst led to the identification of a hydrogen-bonded SC (I), coordinatively-bonded SC(II), carbonyl-bonded SC (III), acrolein, and acrylate SC (IV).[58]

The hydrogen-bonded complex does not take part in the reaction; it is weakly bonded with the surface and is removed after brief pumping at room temperature. Prolonged standing at 25 °C, or increase of the temperature to 100 °C, converts the surface complex (II) into SC (III), an unsymmetrical acrylate which is converted into the symmetrical acrylate SC (IV) with further increase in temperature.

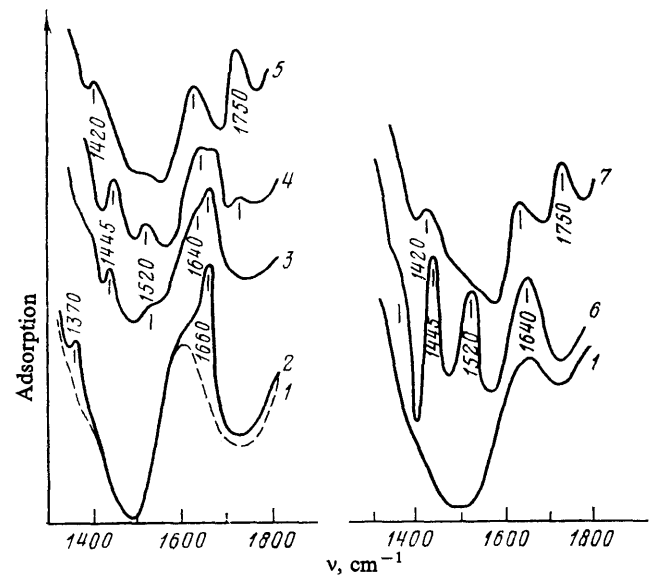


Figure 3. IR spectra of the initial V–Mo–Si–O-catalyst (*1*) and with passage of the reaction mixture containing 0.2 vol.% C_3H_4O; 0.4 vol.% O_2; 99.4 vol.% He at 25 (*2*), 125 (*3*), 160 (*4*), and 280°C (*5*) and after adsorption of acrylic acid at 80 °C (*6*) and 280 °C (*7*).[62]

Under the conditions of the catalytic reaction, with partial oxidation on a V–Mo–O-catalyst, in the temperature range 75–300 °C, the method of high-temperature IR spectroscopy *in situ* identified three surface complexes: coordinatively bonded acrolein (II), acrylate IV) and a molecular form of the adsorbed reaction product, acrylic acid (VII).[61,62]

Because of the high rate on conversion of SC (III) into (IV) under the conditions of reaction it is not possible to observe the change in concentration of SC (III).

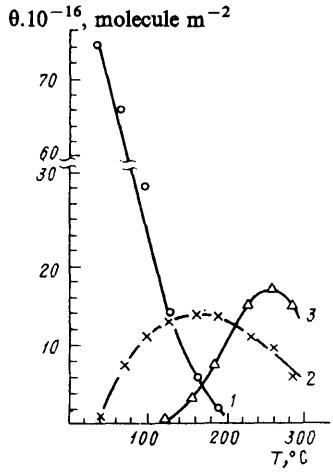


Figure 4. Dependence of the stationary concentrations of SC (II) (curve *1*), (IV) (*2*), and (VII) (*3*), on reaction temperature.[62]

Fig. 3 presents the IR spectra which are obtained by passing the reaction mixture, containing acrolein, through a reaction cell with the V–Mo–Si–O-catalyst, and after the adsorption of acrylic acid. In the temperature range up to 100 °C, only the σ-complex of acrolein [SC (II)] is formed on the surface: $\nu_{C=O}$ = 1660, $\nu_{C=C}$ = 1620, δ_{C-H} = 1370 cm^{-1} (Fig. 3, spectrum *2*). With increase of the temperature to 160 °C, the intensities of the absorption bands at 1370 and 1660 cm^{-1} decrease and absorption bands appear, related to acrylate [SC (IV)]: $\nu_{C=C}$ = 1640, $\nu_{as\,COO^-}$ = 1520, $\nu_{s\,COO^-}$ = 1445 cm^{-1} (Fig. 3, spectra *3* and *4*). Further increase in temperature to 250 °C leads to a decrease in intensity of the absorption bands characteristic of acrylate, and to the appearance of absorption bands at 1420 and 1750 cm^{-1} (Fig. 3, spectrum *5*), which are caused, in our opinion, by re-adsorption on the SiO_2 carrier of acrylic acid, formed at the stage of disintegration of the acrylate. This was confirmed by the formation of SC (VII), by the adsorption of acrylic acid (Fig. 3, spectrum *7*). Acrylate is another surface compound, formed by the adsorption of acrylic acid on the V–Mo–Si–O-catalyst (Fig. 3, spectrum *6*).

The dependence of the stationary concentrations of surface complexes of acrolein on reaction temperature is given in Fig. 4.

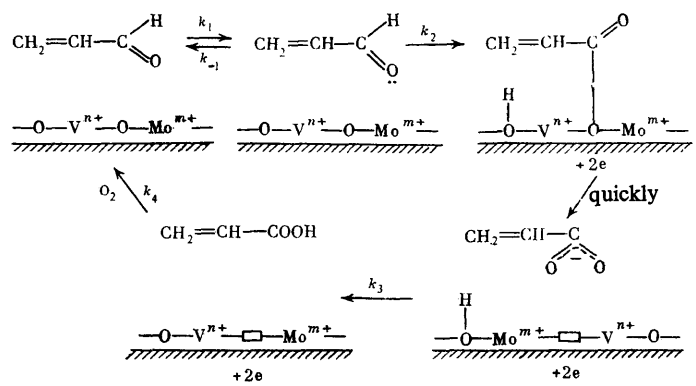
In order to resolve the question of the participation of the observed SC in the course of reaction, a comparsion was made of the rates of formation of reaction products and the rates of destruction of the SC (Table 5). On the basis of such a comparison, it was concluded that acrylic acid is formed by decomposition of the surface acrylate. In the temperature range for which the re-adsorption of acrylic acid on SiO_2 [SC (VII)] is observed, the rate of formation of acrylic acid is close to the sum of the rates of decomposition of SC (IV) and SC (VII).

The active component of the investigated V–Mo–Si–O-catalyst is the chemical compound VMo_3O_{11}, in which vanadium is found in the V^{4+} state and the charge on Mo is close to 6+.[63] It has been shown[58] that the centres of stabilisation for SC (II) on this catalyst are the molybdenum ions, but the centres of stabilisation for acrylate are V^{4+} ions.

Table 5. Comparison of the rates of formation of products of desorption and decomposition of surface compounds.

T, °C	Stationary concentration of SC, $\theta.10^{-16}$ molecule m^{-2}			Rate of decomposition of SC, $W.10^{-14}$ molecule $m^{-2}\,s^{-1}$			Rate of formation desorption products, $W.10^{-14}$ molecule $m^{-2}\,s^{-1}$	
	(II)	(IV)	(VII)	(II)	(IV)	(VII)	$C_3H_4O_2$	$CO+CO_2$
125	14.6	11.3	trace	4.5	0.4	–	0.5	trace
190	2.5	13.0	8.0	–	0.6	0.3	1.1	0.03
230	trace	11.0	16.0	–	1.0	1.4	2.7	0.08
260	–	8.0	17.3	–	1.2	2.2	4.7	0.20
285	–	5.0	14.0	–	0.5	5.2	7.2	0.30

The stated mechanism for the formation of acrylic acid on a V–Mo–Si–O-oxide catalyst can be presented as follows:



A study[62] has been made of the kinetics of conversion for the SC of acrolein, and a non-stationary kinetic model was proposed for the oxidation of acrolein to acrylic acid on a V–Mo–Si–O-catalyst, describing the change in concentration of the SC and the gaseous components of the reaction mixture with time in the temperature range 25–300 °C.

Values of rate constants for the separate stages are given below:

$$k_1 = 23\ atm^{-1}\cdot s^{-1};\ k_{-1} = 1.0\cdot 10^2 \exp\left(-\frac{10\,000}{RT}\right) s^{-1};$$

$$k_2 = 4.5\cdot 10^6 \exp\left(-\frac{19\,000}{RT}\right) s^{-1};$$

$$k_3 = 2.1\cdot 10^3 \exp\left(-\frac{13\,000}{RT}\right) s^{-1};$$

$$k_4 = 1.8\cdot 10^{-14} \exp\left(-\frac{8000}{RT}\right) m^2.molecule.atm^{-1}s^{-1}.$$

Thus, the first stage of reaction in the oxidation of acrolein on a V–Mo–Si–O-catalyst is a donor-acceptor type interaction, with transfer of an electron pair to a vacant orbital of the highly charged and electronegative Mo^{n+} cation. The formation of the σ-complex (II) is accompanied by activation of the C–H bond which undergoes heterolytic fission in the presence, on the surface, of nucleophilic oxygen, with formation of a fragment $(CH_2=CH-C=O)^-$ possessing a formal charge $Q = -1$. This fragment is a good electron donor and restores the catalyst by sharing the electrons of the carbonyl group, with consequent formation of an electrophilic species $(CH_2=CH-C=O)^+$. Calculation shows that the positive charge is almost totally localised on the carbon of the carbonyl group ($Q = 0.8$),[58] so that the species is highly reactive to nucleophilic attack by oxygen of the catalyst, leading to the formation of SC (III). The change from SC (III) to (IV), a symmetrical acrylate with equivalent oxygen atoms, does not apparently present energetic difficulties and occurs rapidly. Decomposition of the surface acrylate (IV), resulting in the formation of acrylic acid, is the slowest step. This mechanism is also confirmed by experimental data, obtained for the stationary state in the course of the reaction. The corresponding kinetic equation:[64]

$$W_{aa} = k_1 C_{acr}/(1 + k_2 C_{acr} + k_3 C_{acr}/C_{O_2}) ,$$

where C_{acr} and C_{O_2} are the concentrations of acrolein and oxygen respectively, describe the experimental data well over a wide range of temperatures and concentrations.

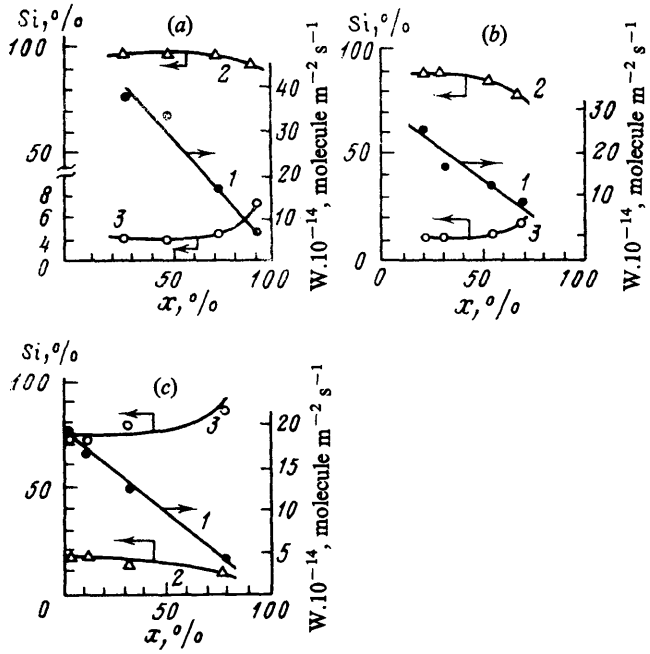


Figure 5. Dependence of catalyst activity (*1*), and its selectivity for C_3H_4O (*2*) and CO + CO_2 (*3*), on the extent of conversion of acrolein at 260 °C, on: *a*, $V_2O_5.3MoO_3/SiO_2$; *b*, β-$CoMoO_4$; *c*, α-$CoMoO_4$.[24] Composition of the reaction mixture: 0.2 vol.% C_3H_4O; 0.4 vol.% O_2; 99.4 vol.% He.

IV. Bond energies of intermediate compounds and the direction of acrolein conversion

The formation of coordinatively-bonded acrolein [SC (II)], appears to be the general form of its interaction with oxide catalysts, on the surface of which there are aprotic centres. It is probably the precursor of the other oxidised SC, namely SC (III), (IV), and (V). However, for selective oxidation of acrolein to acrylic acid, it is insufficient that a σ-complex of acrolein should be formed, followed by its oxidation to a surface acrylate by oxygen of the catalyst. As seen in Table 4, surface compounds of types (II), (III), and (IV) may be formed on inactive and unselective catalysts. The direction of conversion of the surface compounds is influenced more decisively by the strengths of their bonds with the centres of stabilisation and the reactivity of oxygen of the catalyst.

The influence of the bond strengths of the surface complexes of acrolein and its oxidation product, acrylic acid, on the direction of the reaction is confirmed graphically, by comparison of the catalytic properties of vanadium– and cobalt–molybdenum catalysts, and also by their thermal desorption data.[58]

Fig. 5 shows the dependence of the selectivity of these catalysts for acrylic acid and products of deep-seated oxidation, on the conversion of acrolein. The reactions in all cases are described by the consecutive-parallel scheme (Scheme 1) and by first order equations, so that it is possible to express the initial selectivity (S^0) and the constant of (further) oxidation (*b*) as follows:

$$S^0_{aa} = \frac{k_1}{k_2 + k_1} , \quad S^0_{CO+CO_2} = \frac{k_2}{k_1 + k_2} , \quad b = \frac{k_3}{k_1 + k_2}$$

Table 6. Catalytic properties of various catalysts for the oxidation of acrolein (composition of the reaction mixture, vol.%: C_3H_4O—0.2%, O_2—0.4%, He—99.4%, reaction temperature—260 °C.

Chemical composition	Specific surface $m^{-2}\,g^{-1}$	Reaction rate, $W.10^{-14}$, molecule $m^{-2}\,s^{-1}$, for x=50%		Initial selectivity %		Further oxidation constant, *b*, mol fraction
		Overall conversion of acrolein	Formation of acrylic acid	$C_3H_4O_2$	$CO+CO_2$	
$V_2O_4 \cdot 9MoO_3/SiO_2$	44.0	8.85	8.43	96.0	4.0	0.01
β-$CoMoO_4$	9.0	14.60	11.00	88.0	10.0	0.04
α-$CoMoO_4$ *	9.0	8.20	0.97	18.0	75.0	0.20
$V_{0.05}Sb_{0.95}$ **	78.0	0.53	0.20	90.0	10.0	1.70

*Acetic acid present in the reaction products.
**Reaction temperature 300 °C.

In Table 6, the values of S^0_{aa} and *b* are given for the catalysts under investigation. In Fig. 6, the results of chromatographic analysis are shown for the products of thermal desorption for acrolein (Fig. 6*a*) and acrylic acid (Fig. 6*b*) on the V–Mo–Si–O-catalyst.[24] In both cases, in the temperature range 70–350 °C, the

desorption of acrolein and acrylic acid is not accompanied by destruction of the carbon skeleton. In the 350–500 °C region the products of thermal desorption are CO and CO_2. On α- and β-$CoMoO_4$, the thermal desorption curves have a similar appearance, yet acetaldehyde and acetic acid are also present among the products of decomposition.[24]

In Fig. 7*a*, the initial selectivities for acrylic acid and for products of deep-seated oxidation are compared with the relative amounts of the weakly sorbed (T_{des} = 70–350 °C) and strongly sorbed (T_{des} = 350–500 °C) acrolein (θ^{acr}_{weakly} and $\theta^{acr}_{strongly}$ respectively), and Fig. 7*b* shows the dependence of the further oxidation constant (*b*) on the relative amount of strongly sorbed (T_{des} = 350–500 °C) acrylic acid. The correlation of these values clearly indicates the participation of a weakly bonded form of acrolein in the formation of acrylic acid, but strongly bonded forms of acrolein and acrylic acid in the formation of products of destructive oxidation by parallel and consecutive pathways. The proportions of these forms also determine the selectivity. It should be noted that revelation of such a clear correlation was favoured by the purely fortuitous closeness of the bond energies for oxygen on these catalysts (see Table 1).

From Figs. 4 and 6*a*, it follows that the weakly bonded forms of acrolein are coordinatively-bonded acrolein [SC (II)] and acrylate [SC (IV)]. The structure of strongly bonded acrolein on the V–Mo–Si–O-catalyst could not be identified by IR spectroscopy, the amount being very small because of the high selectivity of the catalyst.

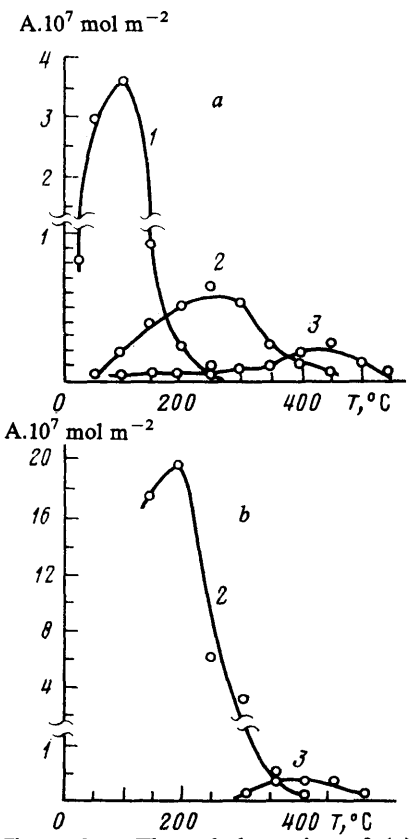


Figure 6. Thermal desorption of (*a*) acrolein and (*b*) acrylic acid with V–Mo–Si–O-catalyst.[24] *1*, acrolein; *2*, acrylic acid; *3*, CO + CO_2.[24]

Surface compounds of the acrylate type are formed by the adsorption of acrylic acid on both selective and non-selective catalysts for the oxidation of acrolein (see Table 4). It has been shown[65] that the properties of the surface acrylates, in particular the strength of the bond with the surface, can be judged by the temperature of decomposition by thermal desorption, and that the composition of the products of desorption on various catalysts differ considerably. Weakly bonded arylates that are formed for example, by the adsorption of acrylic acid on the V–Mo–O-catalyst and on MoO_3, are decomposed by an increase in temperature to 200 °C, with release of acrylic acid into the gas phase. Acrylate, formed on MgO, is strongly bonded with the surface and undergoes practically no change up to 400 °C. Further increase in the temperature leads to its destructive oxidation to give surface carboxylate, containing no C=C bond [SC (V)], and further decomposition occurs above 500 °C with release into the gas phase of acetic acid, acetaldehyde, and oxides of carbon. On CuO, a typical catalyst for deep-seated oxidation, further oxidation of the surface acrylates occurs at only 200 °C to give carbonato-carboxylate complexes, which decompose at 250 °C with the release into the gas phase of oxides of carbon. The low temperature at which further oxidation of SC (IV) occurs in this case is due, apparently, to the presence of weakly bonded oxygen in CuO.

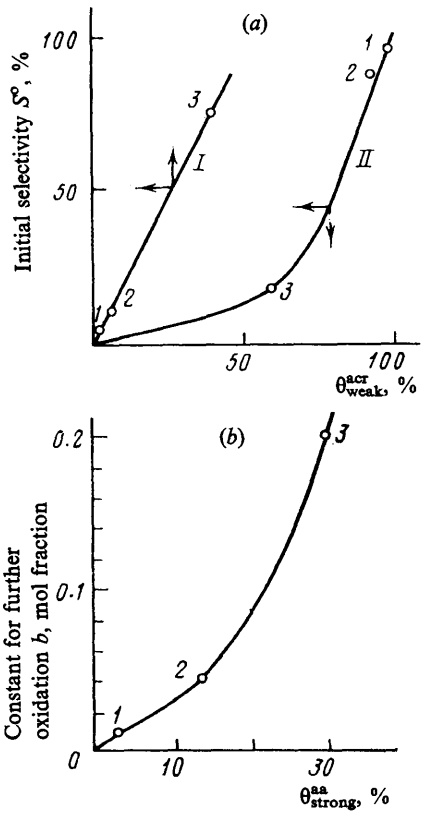


Figure 7. Dependence of initial selectivities for strongly adsorbed acrolein (curve *1*), and for acrylic acid (curve *2a*) in relation to weakly adsorbed acrolein; and the dependence of the constant for further oxidation on the relative quantity of strongly adsorbed acrylic acid (*b*). Catalysts used: *1*, $V_2O_5.9MoO_3/SiO_2$; *2*, β-$CoMoO_4$; *3*, α-$CoMoO_4$.

Thus, from all accounts, it follows that the bond strength of the intermediate surface compounds determines the direction of conversion of acrolein, but the simultaneous requirement of high activity and selectivity dictates that the SC should have an optimum bond energy. Evidently, the higher the bond energy of oxygen and the lower the bond strength of the SC of the adsorbed acrolein, the more selective the catalyst but the lower is its activity.

In Table 7 the heats of adsorption are given for acrolein and acrylic acid on promoted V–Mo–O-catalysts, measured *in situ* by a calorimetric method[66] together with the heats of adsorption for oxygen.[42]

Table 7. Catalytic properties of modified V–Mo-oxide samples, supported on SiO_2 (70 mass% SiO_2).

Composition of active material	$W.10^5$, mol m^2 h^{-1} for $x=70\%$	S^o_{aa}, %	Further oxidation constant, b mol fraction	Heat of adsorption, q kJ mol^{-1}		
				C_3H_4O [66]	$C_3H_4O_2$ [66]	O_2 [42]
$V_2O_4 \cdot 9MoO_3$	10.6	96.5	0.011	84	75	255
$V_2O_4 \cdot 9MoO_3 \cdot 1CuO$	12.3	98.3	0.005	84	75	226
$V_2O_4 \cdot 9MoO_3 \cdot 0.2Cs_2O$	0.3	97.5	0.058	84	96	326
$V_2O_4 \cdot 9MoO_3 \cdot 0.06P_2O_5$	6.3	88.0	0.014	117	75	335
$0.5 \cdot V_2O_4 \cdot 9MoO_3 \cdot 0.5SiO_2$	10.6	97.0	0.007	–	75	274

As seen from Table 7, the most active and selective catalysts (the binary and copper-promoted V–Mo–O-catalyst) are characterised by heats of adsorption q_{O_2} = 230–250, q_{acr} = 75, and q_{acr} = 84 kJ mol^{-1}. These values are apparently close to the optimum.

The influence of the energetic characteristics of the intermediate compounds on the rate of formation of acrylic acid on V–Mo-catalysts can be seen from Fig. 8. The slow stage of the oxidation reaction of acrolein is desorption of acrylic acid.[62,64] In accordance with the Brønsted–Polanyi equation, the rate of formation of acrylic acid is described by the following expression:

$$W_{aa} = A \exp \frac{-\alpha q_{aa} - \beta q_{O_2}}{RT} [V^{4+}],$$

where $A = k_0 \exp(-E_0/RT)$. The applicability of this equation is confirmed by Fig. 8. A coincidence is observed between the experimentally found number of V^{4+} centres for the stabilisation of acrylate and that calculated from the given equation, with $\beta = 0.07$ and $\alpha = 0.4$. These values for the coefficients α and β correspond to the limiting stage of the reaction; they allow a judgement to be made about the relationship of oxidation-reduction (β) and acid-base (α) properties of the catalyst.

From the mechanism of reaction we turn to a consideration of the principles underlying the choice of catalyst for the oxidation of acrolein to acrylic acid. The basic factor which determines the direction of reaction is the energy of the bond with the SC. Acrolein and the product of its oxidation, acrylic acid, differ in acidic properties and it is therefore possible to influence the strengths of the bonds of the intermediate compounds by regulation of the acid-base properties of the catalyst. For a selective course of reaction, optimum acidity is required: on the one hand, it is necessary to ensure the possible adsorption of acrolein as an organic base with a high velocity of conversion but on the other, to prevent the re-adsorption of acrylic acid to avoid further oxidation. Increase in the acidity above the optimum, gives rise to the formation of a strongly bonded SC of acrolein and leads to an increase in the proportion of products of deep-seated oxidation which are formed by a parallel route, lowering the initial selectivity for acrylic acid. A multistage mechanism for the formation of acrylic acid assumes the existence, in selective catalysts, of a number of centres, differing in their donor–acceptor properties and in their ability to form weakly bonded σ-complexes of acrolein (II) and acrylate (IV).

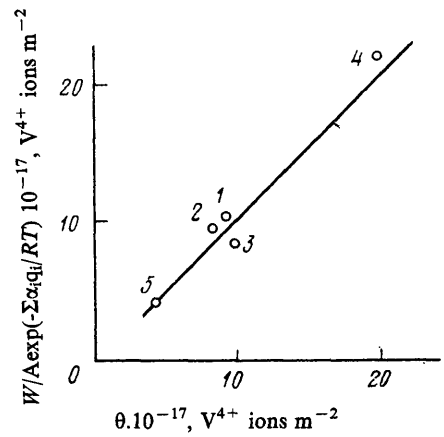


Figure 8. Comparison of the calculated and experimental numbers of V^{4+} centres. Catalysts used: *1*, $V_2O_4.9MoO_3/SiO_2$; *2*, $V_2O_4.9MoO_3.1CuO/SiO_2$; *3*, $0.5V_2O_4.9MoO_3.0.5TiO_2/SiO_2$; *4*, $V_2O_4.9MoO_3.0.06P_2O_5/SiO_2$; *5*, $V_2O_4.9MoO_3.0.2Cs_2O/SiO_2$.

Since acrylate, i.e. the surface complex from which acrylic acid is formed spontaneously, is a salt-like compound, the optimum composition of the catalyst must include elements such as V^{4+}, Mo^{4+}, or Ti^{4+}, which possess amphoteric properties in the oxidation state that is realised under reaction conditions. At the same time, the first stage, the formation of a σ-complex of acrolein, [SC (II)], requires the catalyst to contain highly electronegative ions of the Mo^{6+} type. Nevertheless, an important requirement for catalyst selectivity is the presence of oxygen with a sufficiently high energy bond. Although oxygen participates in all stages of conversion of the surface compounds, its energetic characteristics in the first place affect the stage at which the σ-complex undergoes conversion, since it is precisely on this that the subsequent structure of the SC depends: oxygen, possessing high reactivity, forms surface complexes with high oxygen content, thus promoting the destruction of adsorbed molecules and, consequently, their non-selective conversion. The sum total of these conditions also determines the influence of the acid-base and oxidation-reduction properties. The catalyst which best satisfies these requirements is the V–Mo–O-catalyst, which has energetic characteristics (q_{O_2}, q_{aa}, q_{acr}) that are apparently near to the optimum.

Knowledge of the detailed reaction mechanism allows the catalytic properties of the sample to be changed by the introduction of appropriate additives. Thus, the V–Mo–O-catalyst, on which the limiting stage of reaction is the conversion of the surface acrylate, can be improved by the introduction of a weakly basic additive such as Cu.[67] The introduction of strongly basic additives (Cs, Na, K) or an acidic additive, P, causes a sharp deterioration in the properties.[68] On the contrary, for the V–Sb–O-catalyst, the surface of which does not contain highly electronegative ions, the limiting stage is the formation of coordinatively-bonded acrolein [SC (II)].[69] This catalyst is improved significantly by the introduction of acidic additives, for example phosphorus:[70] its activity is increased and its selectivity is also increased, on account of the suppression of further oxidation of the acrylic acid.

The optimum combination of acid-base and oxidation-reduction properties may only be achieved by the use of a multi-component catalyst. This is confirmed by the low efficiency of individual oxides for the formation of acrylic acid.[40] Molybdates of group II metals of the periodic system[28] are also far from being optimum catalysts: with the reaction proceeding by the mechanism described above, acrylate must be stabilised on these compounds at highly basic ions, i.e. it must be strongly bonded with the surface; this, however, favours an increase in the temperature of the catalyst and destruction of the acrylate, as observed experimentally.

It should be noted that the views described here indicate only the general direction of the search for the chemical composition of a catalyst. In each particular case it is necessary to take account of the structure, coordination sphere, valency state, and proportions of the chemical elements in the catalyst, since these are all reflected in the oxidation-reduction and acid-base properties which determine the structure and strength of the various surface compounds. The examples of α- and β-$CoMoO_4$ are object lessons in this respect. These two polymorphous modifications, differing in the coordination of the Mo, and in the presence of Co^{3+} ions in α-$CoMoO_4$ but not in β-$CoMoO_4$, possess different catalytic properties in the reaction of acrolein oxidation:[24] α-$CoMoO_4$ in practice is a catalyst for the deep-seated oxidation of acrolein, but β-$CoMoO_4$ is a selective catalyst.

In conclusion, it should be noted that the oxidation of acrolein to acrylic acid is not an exception in the large number of reactions of partial oxidation. The role of the acid-base and oxidation-reduction properties of the catalyst in such reactions was shown for the first time in an earlier publication[71] and later by other workers.[72,73] At the present time, it is suggested that reactions and catalysts should be classified by their type of acid-base and oxidation-reduction activity.[74]

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