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Adsorption of ethanol on the modified ruthenium catalysts in alkaline media

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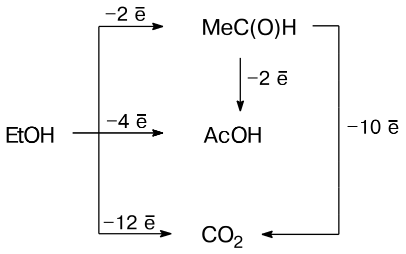
Regularities of ethanol adsorption in alkaline medium on the surface of the monoruthenium Ru/C catalyst and systems promoted by nickel and vanadium oxides, Ru—VO_x/C and Ru—NiO_x/C, were studied by non-stationary voltammetry techniques. An analysis of the kinetic and concentration dependences of adsorption showed that an increase in the content of the promoting component in the bimetallic systems enhances the energy heterogeneity of the catalyst surface. The data on adsorption measurements were compared with the results of previous studies of the kinetics and depth of ethanol electrooxidation on the examined catalysts. The larger quantity of electricity consumed for the oxidation of adsorbed particles formed on the surface of the metallooxide systems corresponds to higher extents of electrooxidation and rate than those for the monoruthenium catalyst.

Key words: electrocatalysis, bifunctional catalysis, ethanol adsorption, depth of ethanol electrooxidation rate, platinum-free catalysts, Temkin equation, Roginskii—Zel´dovich equation, irregularity factor.

Development of a low-temperature fuel cell (FC) is aimed at producing an enronmentally safe electric generator with high efficiency. Ethanol is one of the most promising fuels for this type of FC. To operate the ethanolic FC with the maximum efficiency, each alcohol molecule has to transfer 12 electrons to the external chain per one current producing reaction. However, the electrooxidation of ethanol on the platinum catalysts includes the chain of consecutive and parallel reactions (Scheme 1) leading, as a rule, to the predominant formation of acetaldehyde (two-electron mechanism) and acetic acid (four-electron mechanism).

Scheme 1



The low values of depth and total rate of ethanol electrooxidation on platinum are due to the formation of strongly chemisorbed substances (SCS) on the catalyst surface. One of the way of improving the characteristics of an ethanolic FC is the development of modified electrocatalytic systems. Polymetallic catalysts based on platinum group metals can provide a higher rate of ethanol oxidation due to the effect of bifunctional catalysis.[1] Alcohol molecules are adsorbed and dehydrogenated on the sites of the active components of the catalyst (Pt or Pd), whereas the promoting component serves as a donor of active oxygen providing the reoxidation of SCS at low anodic potentials. The system PtSn is considered[2—4] to be the most efficient electrocatalyst for ethanol oxidation in acidic electrolytes. At the same time, in alkaline media the depth and rate of ethanol electrooxidation can increase due to an increase in the deprotonation rate of adsorbed alcohol molecules and participation of ions OH^- in the reaction (Scheme 2).

Scheme 2

$$HCO_{ads} + 2\,OH_{ads} + OH^- \longrightarrow CO_2 + 2\,H_2O + e^-$$

In addition, the possibility of successful use of catalysts with less expensive Pd and Ru instead of platinum and various promoting components[5—9] in the synthesis of binary systems (NiO_x, FeO_x, VO_x,[5,6] as well as MgO, CeO_x, ZrO_x (see Ref. 7)) was shown.

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The nature of the electrode affects the rate and selectivity of alcohol electrooxidation, since the adsorption energy, composition of the adsorption layer, and coverage of the surface with adsorbed particles change depending on the electrode. Therefore, the study of the regularities of adsorption of organic fuel on the surface is important in investigation of the properties of the electrocatalyst. A complex of electrochemical[10—16] and analytical[17—19] methods of studying adsorption and electrooxidation of alcohols on platinum group metals has been developed to the present time. The methods based on measuring the quantity of electricity necessary for oxidation or reduction of the adsorbate and the indirect method of adsorption displacement are most popular among the electrochemical methods. In the adsorption displacement method, the measure of adsorption of the studied compound is a decrease in adsorption of other particles (as a rule, hydrogen) compared to the supporting electrolyte in the presence of the studied compound. Although the process of alcohol adsorption is accompanied by the destruction of alcohol molecules, it can formally be described by the equations obtained from the statistical approach to the process of reversible adsorption on nonuniform surfaces.[20] However, the irreversible character should be taken into account when interpreting these dependences of adsorption on the alcohol concentration and duration of its contact with the electrode (*i.e.*, kinetic and concentration dependences).

Adsorption of ethanol in an alkaline medium on the surface of platinum[13,21,22] and rhodium[23] has received an increased attention. Along with the electrochemical methods, diverse analytical methods of investigation were also used: chromatographic analysis,[13,22] method of radioactive indicators,[21] and potential-modulated reflectance spectroscopy.[23]

The purpose of the present work is the study of specific features of the ethanol absorption process in an alkaline medium on the ruthenium catalyst and bimetallic systems Ru—VO_x and Ru—NiO_x. The work was aimed at determining the dependence of the adsorption characteristics on the alcohol concentration, duration of adsorption, and catalyst composition.

Experimental

The catalysts based on ruthenium was synthesized on the carbon support, carbon black XC-72 (specific surface 275 $m^2 g^{-1}$) by the reduction of precursors (ruthenium and vanadium salts) in a hydrogen atmosphere at 450 °C. The procedure of synthesis of the catalysts has earlier been described in detail.[5,6,24—26] According to the published results of structural analyses by XPS, X-ray diffraction, and transmission electron microscopy,[5,6,24] ruthenium in the catalyst Ru/C exists as metal. In the composition of the multicomponent systems Ru—VO_x and Ru—NiO_x, the ruthenium atoms are decorated by vanadium and nickel oxides, respectively, of variable composition. The weigh fractions of the components presented were calculated from the ratio of the amounts of precursors ignoring the fraction of oxygen incorporated in the catalyst. The composition of the catalyst $Ru_{60}V_{40}O_x/C$ (20 wt.% (Ru + V)) chosen for the present study corresponds to the composition optimal from the viewpoint of the highest activity during ethanol electrooxidation. The dependence of parameters of ethanol adsorption on the composition of the active phase of the catalyst was studied for the system Ru—NiO_x/C (15 wt.% (Ru + Ni)).

Electrodes were prepared by supporting a mixture of the catalyst and Nafion as a binder (20 wt.% based on dry substance) on the nickel lattice with a geometric surface of 1 cm^2. The amount of the supported catalyst was monitored gravimetrically, and it was 1±0.1 mg. Adsorption processes were studied in a standard electrochemical cell in a solution of 1 *M* KOH + 0.2 *M* EtOH at 60 °C. The mercury—mercuric oxide electrode served as a reference. Reagents of special purity grade and bidistilled water were used for the preparation of solutions. Prior to experiments, the working space of the cell was deaerated with argon (special purity grade) for 30 min.

The time (kinetic) and concentration dependences of ethanol adsorption were studied. The specific characteristics of the catalysts were calculated from the values of active surface of the metallic phase determined by the method of carbon monoxide desorption in a 1 *M* KOH deaerated solution at 60 °C. The solution was saturated with CO for 30 min at the electrode potential 0.04 V (hereinafter the potentials are presented relative to the reversible hydrogen electrode in a 1 *M* KOH solution). Then CO excess was purged away in the cell with an argon flow (40 min), and anodic potentiodynamic curves were detected in the potential region 0.04—1 V with a potential sweep rate of 50 $mV s^{-1}$. The value of specific surface of the active phase of the catalysts (S_{CO}) was determined from the quantity of electricity under the maxima of the curves corresponding to desorption of hydrogen and carbon monoxide (Fig. 1). The content of the metals (Ru + Ni) and Ru in the catalyst—support system is 15 wt.%, and that of (Ru + V) is 20 wt.%.

Catalyst	S_{CO}/m^2 (g of Ru)$^{-1}$
Ru	100
$Ru_{60}V_{40}$	45
$Ru_{92}Ni_8$	32
$Ru_{84}Ni_{16}$	21
$Ru_{68}Ni_{32}$	23
$Ru_{58}Ni_{42}$	6
$Ru_{37}Ni_{63}$	10

The ratio of the surfaces areas of maxima of the desorption curves $Q_{CO}/Q_H \approx 2$ suggests the linear character of CO adsorption on these systems, which corresponds to a quantity of electricity of 0.42 mC cm^{-2} necessary for removal of the CO monolayer from the catalyst surface.

Two approaches to determination of the coverage of the catalyst surface with adsorbate were compared when ethanol adsorption was studied: (1) the values of coverage of the surface with organic particles were normalized on the basis of a decrease in the amount of hydrogen adsorbed in the presence of ethanol; and (2) the values of coverage were normalized on the basis of the quantity of electricity consumed for the oxidation of ethanol during an anodic pulse measured after adsorbate accumulation on the catalyst surface.

Typical changes in the character of the anodic polarization curve in the region of hydrogen desorption and oxidation of

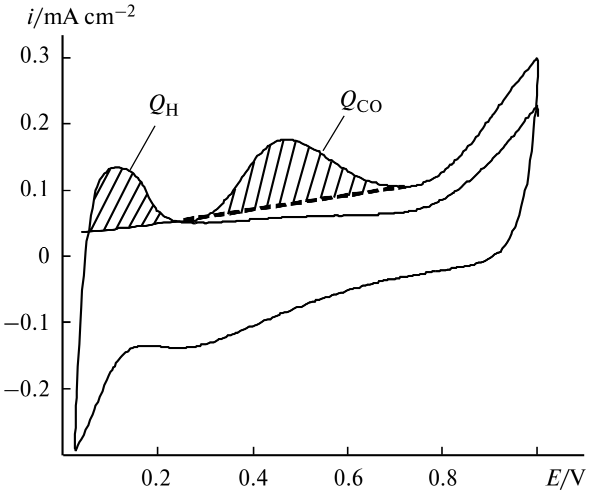

Fig. 1. Curve of CO desorption and voltammetry in the supporting electrolyte on the catalyst Ru—VO$_x$/C. The data based on 1 cm^2 of the Ru surface are presented here and in Figs 2, 5, 7, and 9.

adsorbed organic particles with an increase in the duration of adsorption are presented in Fig. 2. As shown by arrows, the value of current decreases upon hydrogen desorption and increases upon the oxidation of organic particles. The both methods used for determination of coverages are based on the analysis of the experimental dependences of this type.

In the framework of the first method, the coverage was determined by the equation

$$\theta = (Q_H{}^b - Q_H{}^{EtOH})/Q_H{}^b, \quad (1)$$

where θ is the coverage of the surface; and $Q_H{}^b$ and $Q_H{}^{EtOH}$ are the charges needed to remove the monolayer of adsorbed hydrogen in the absence and in the presence of ethanol in solution, respectively.

The values of Q_H were calculated from the anodic curves measured after ethanol adsorption during specified time (see Fig. 2):

$$Q_H = Q^i - Q_0{}^i, \quad (2)$$

where Q^i is the current value of the charge of the measured anodic curve at the potential 0.33 V. The high value of $Q_0{}^i$ corresponding to the complete displacement of adsorbed hydrogen is due to the polarization capacity of the carbon support, which is characterized by high specific surface.

In the calculation of the coverage of the electrode surface according to the second method, the measure of surface coverage was the surface area under the maximum of adsorbate oxidation ($Q_{0.9}{}^{EtOH(i)}$) in the potential range from 0.33 to 0.90 V (see Fig. 2). The coverage of the surface was determined as follows:

$$\theta = Q_{0.9}{}^{EtOH(i)}/Q_{0.9}{}^{EtOH(m)}, \quad (3)$$

where $Q_{0.9}{}^{EtOH(m)}$ is the maximum charge at a potential of 0.9 V achieved under the chosen conditions of investigation of adsorption. According to the accepted assumption, the value of $Q_{0.9}{}^{EtOH(i)}$ referred to the first anoldic pulse comprises the same fraction from the charge corresponding to the complete oxidation of particles adsorbed on the electrode surface under any experimental conditions.

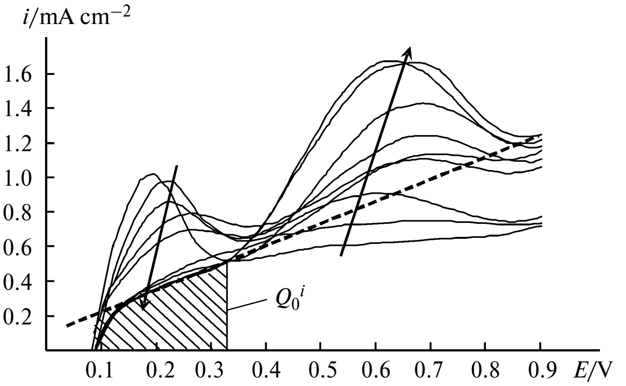

Fig. 2. Change in the character of anodic pulses on the catalyst Ru—VO$_x$/C after increasing time intervals of ethanol adsorption at a potential of 0.08 V. Arrows show how the course of curves changes with increasing duration of adsorption; 1 M KOH + 0.2 M EtOH, potential application rate 500 mV s^{-1}.

The overall shape of potential sweep used in adsorption measurements is presented in Fig. 3. Region *A* corresponds to the process of preliminary treatment of the electrode, which was carried out to remove organic particles from the surface, region *B* corresponds to the period of ethanol adsorption (0.1—2500 s), and region *C* corresponds to the measurement of the potentiodynamic anodic pulse. The potential of accumulation of organic particles (0.08 V) approximately corresponded to the stationary potential established on the studied catalysts in 1 M KOH solutions with an alcohol concentration of 0.1—2 mol L^{-1} at 60 °C. The absence of adsorbed organic species on the electrode is confirmed by coincidence of the voltammetric curves measured in the absence and in the presence of ethanol in the potential range 0.08—0.9 V. The electrode was cleaned only at low concentrations of alcohol (≤0.2 mol L^{-1}). Therefore, for measurement of the kinetic dependences of adsorption, we chose the limiting concentration of ethanol (0.2 mol L^{-1}), which makes it possible to remove organic particles from the electrode surface before experiment. When measuring the concentration dependences in the range of alcohol contents 0.001—2 mol L^{-1}, the

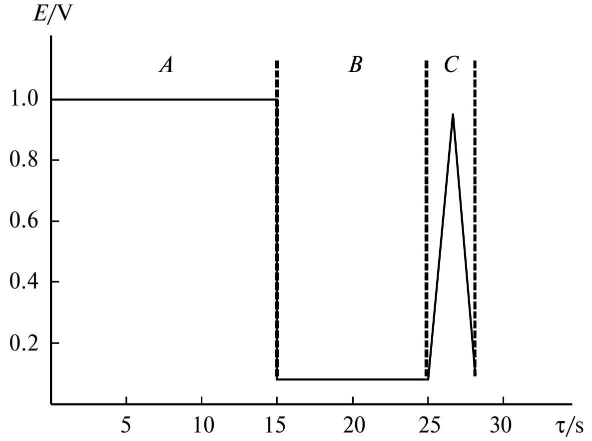

Fig. 3. Shape of the potential scan used in adsorption measurements.

time of adsorption beginning was counted from the moment of immersion of the electrode into the working solution. The value of stationary potential was specified with a potentiostat. The duration of adsorbate accumulation in concentration measurements (1200 s) was chosen taking into account minimization of the influence of adsorption of admixtures in dilute solutions of alcohol. According to the results of preliminary studies, at the electrode polarization >2500 s in the supporting electrolyte (1 *M* KOH) the presence of admixtures results in a noticeable decrease in hydrogen adsorption. This decrease is at most 8—10% when the duration of storage is halved.

In measurement of anodic pulses the potential sweep rate is 100 mV s^{-1} at the alcohol concentrations lower than 0.2 mol L^{-1} and it is 500 mV s^{-1} at higher concentrations. As can be seen from the data presented in Fig. 4, re-adsorption at the sweep rate higher than 500 mV s^{-1} can be neglected even at the alcohol concentration 1 mol L^{-1}. When the alcohol concentration decreases, the sweep rate at which re-adsorption is not observed also decreases.

The measurement of at least one point of the adsorption curve does not result in a decrease in the activity of the electrode, which indicates the absence of its degradation at a potential of 1.0 V. After two and more measurements, the activity decreases noticeably, which indicates the partial degradation of the catalyst.

Results and Discussion

The dependences of Q_H and $Q_{0.9}{}^{EtOH(i)}$ on the duration of ethanol adsorption on the catalyst Ru—VO_x/C are presented in Fig. 5. The amount of adsorbed hydrogen decreases with an increase in the duration of ethanol adsorption. After 1000—1500 s, hydrogen is almost completely displaced from the active sites of the catalyst. After organic particles are accumulated on the electrode during 2500 s, the value of $Q_{0.9}{}^{EtOH(m)} \approx 0.40$ mC cm^{-2} is achieved. Based on changing the values of Q_H and $Q_{0.9}{}^{EtOH(i)}$, the dependences of the surface coverages on the duration of ethanol adsorption were calculated by Eqs (1) and (2) (Fig. 6). As can be seen these curves are rather similar and have the same slope in the region of adsorption time intervals of 20—500 s. One of the possible reasons for their some discrepancy is a low accuracy of determination of the value of Q_H on the metallooxide systems when the adsorption duration exceeds 1000 s. However, if hydrogen adsorption is complicated because the catalyst surface is occupied, certain time (1000—1500 s) is needed to restore stable values of the composition of the adsorption layer and, hence, $Q_{0.9}{}^{EtOH(i)}$. The same slope of the curves measured from hydrogen desorption and oxidation of the organic adsorbate in the region of medium coverages indicates the similar energy of interaction of adsorbed particles with the surface under the given conditions. In addition, satisfactory agreement between the number of adsorption sites liberated from hydrogen and occupied with ethanol is observed.

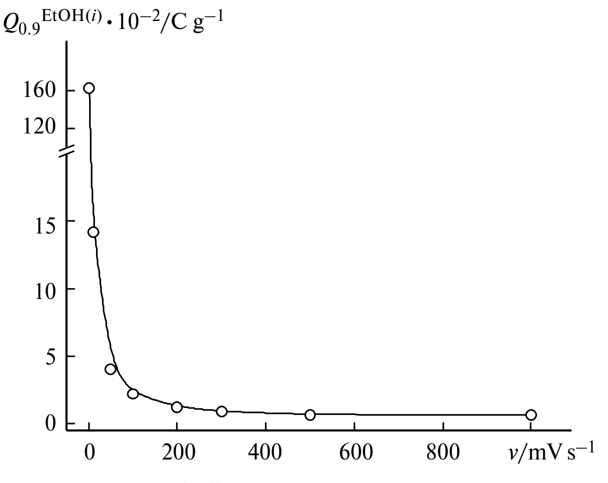

Fig. 4. Plot of $Q_{0.9}{}^{EtOH(i)}$ (based on 1 g of the catalyst Ru—VO_x/C) *vs* potential sweep rate; 1 *M* KOH + 1 *M* EtOH.

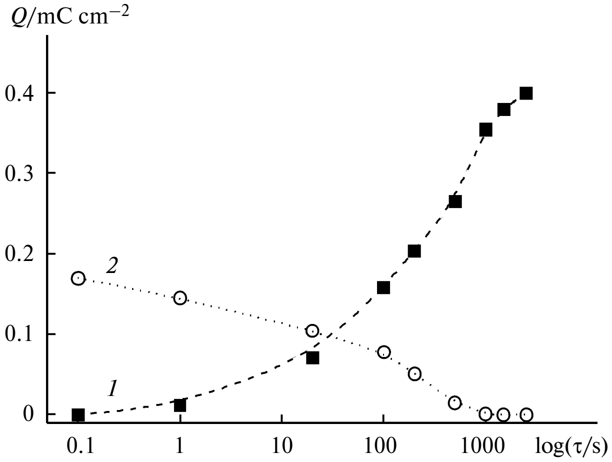

Fig. 5. Plots of $Q_{0.9}{}^{EtOH(i)}$ (*1*) and Q_H (*2*) *vs* duration of ethanol adsorption on the catalyst Ru—VO_x/C; 1 *M* KOH + 0.2 *M* EtOH; here and in Figs 6—9, the abscissa is logarithmic.

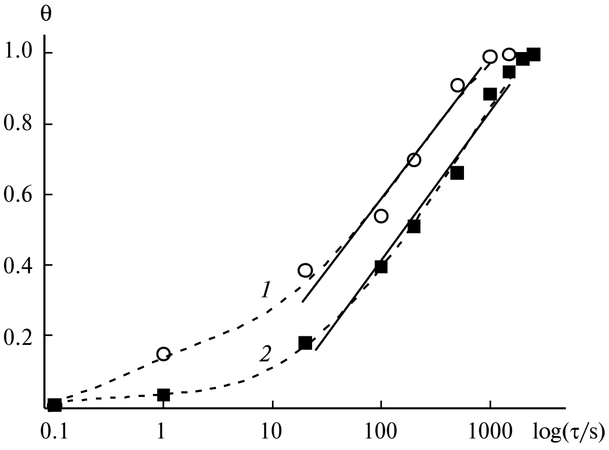

Fig. 6. Time plots of the coverage with ethanol of the Ru—VO_x/C catalyst surface; the coverage was calculated from the change in Q_H by Eq. (1) (*1*) and in $Q_{0.9}{}^{EtOH(i)}$ by Eq. (3) (*2*).

Linear approximation of the regions of the adsorption curves corresponding to medium coverages can be described by the Roginskii—Zel´dovich equation[27] derived for the adsorption kinetics on the evenly nonuniform surface

$$\theta = \mathrm{const} + (\alpha f)^{-1}\ln\tau, \qquad (4)$$

where f is the irregularity factor of the catalyst surface, which reflects the difference between the maximum and minimum values of adsorption energy and characterizes the change in the adsorption energy with coverage; and α is the transition coefficient ($0 < \alpha < 1$). Curves *1* and *2* (see Fig. 6) are characterized by the value $\alpha f \approx 6.6$.

To study the influence of experimental conditions on the measured parameters of adsorption, we also determined the concentration dependences of ethanol adsorption on the catalysts studied (Figs 7 and 8). Discrepancy between the adsorption curves (see Fig. 8) calculated by Eqs (2) and (4) for the concentration dependences at low alcohol concentrations is higher than that for the time dependences, which can be due to the higher degree of dissociative adsorption of ethanol at its low concentrations. This follows, in particular, from the data on the extent of ethanol oxidation on the system considered, according to which the yield of CO_2 increases with a decrease in the alcohol concentration.[6] In the region of medium coverages, curves *1* and *2* are parallel and can formally be described by the Temkin equation of concentration isotherm[20]

$$\theta = \mathrm{const} + f^{-1}\ln c. \qquad (5)$$

The value of factor f in Eq. (4) approximately corresponds to the value of αf for the time dependence of the amount adsorbed with the transition coefficient $\alpha = 1$. The corresponding values of $Q_{0.9}{}^{\mathrm{EtOH}(m)}$ are also similar (0.40—0.42 mC cm^{-2}). These results suggest similarity of the chemical composition and energy state of species adsorbed on the electrode under the conditions of time and concentration measurements of ethanol adsorption at least in the region of medium coverages. In addition, the data presented confirm the possibility to determine the surface coverage with organic particles on the basis of the value of $Q_{0.9}{}^{\mathrm{EtOH}(i)}$. This procedure was used for the study of the adsorption properties of the catalytic system Ru—NiO$_x$/C. The dependence of the parameters of ethanol adsorption on the ratio of amounts of the active (ruthenium) and promoting (nickel oxides and hydroxides) components of the metallic phase of the catalyst was determined for this system.

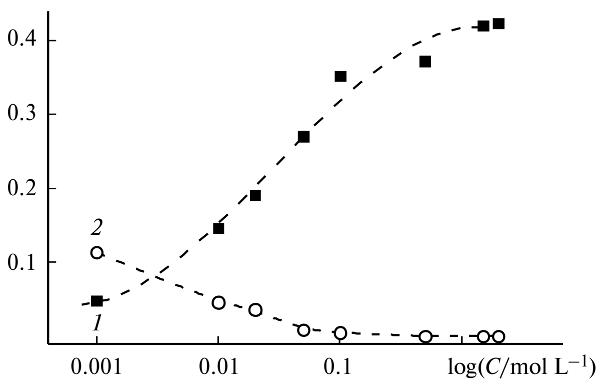

Fig. 7. Plots of $Q_{0.9}{}^{\mathrm{EtOH}(i)}$ (*1*) and Q_{H} (*2*) *vs* ethanol concentration during its adsorption on the catalyst Ru—VO$_x$/C.

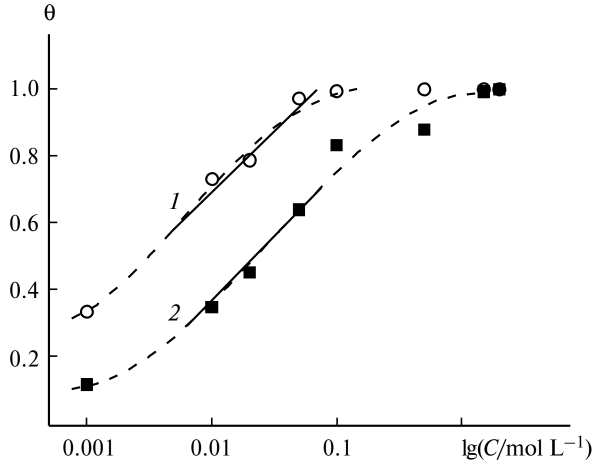

Fig. 8. Concentration plots of the coverage with ethanol of the Ru—VO$_x$/C catalyst surface; the coverage was calculated from the change in Q_{H} by Eq. (1) (*1*) and in $Q_{0.9}{}^{\mathrm{EtOH}(i)}$ by Eq. (3) (*2*). lg(*C*/моль•л$^{-1}$) log(*C*/mol L^{-1})

As shown in Fig. 9, the dependence of the quantity of electricity consumed by the oxidation of adsorbed organic particles on the catalyst composition is described by the curve with a maximum. The maximum charge in the anodic run of the curve is achieved on the catalyst in which the fraction of ruthenium with respect to nickel is 70%, which corresponds to 10.5 wt.% Ru in the system Ru—NiO$_x$/C. The maximum charge decreases with the further increase in the ruthenium content. The variable values of $Q_{0.9}{}^{\mathrm{EtOH}(m)}$ can be explained by the fact that the composition of the metallooxide system affects either the number of accessible adsorption sites on the catalyst surface or the level of alcohol electrooxidation. The first explanation assumes the possibility of ethanol chemisorption on the nickel-containing components of the system. The ability of metallic nickel to adsorb and oxidize ethanol was described.[28—30] At the same time, according to the XPS data,[24] nickel exists predominantly in the oxidized state in the composition of the Ru—NiO$_x$/C system. In addition, as shown above, the surface area of the metallic phase accessible for CO adsorption decreases gradually with an increase in the nickel content in the catalyst. Therefore, the assumption that the extent of alcohol oxidation changes with the composition of the binary catalysts seems more

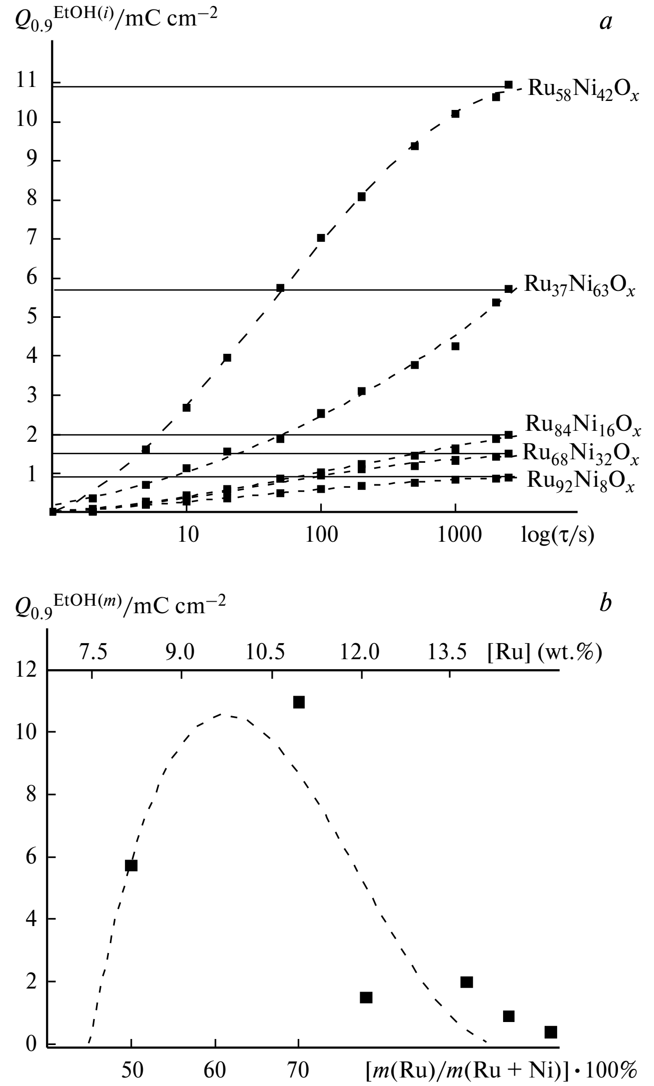

Fig. 9. Ethanol adsorption as a function of time on the catalysts Ru—NiO$_x$/C (15 wt.% (Ru + Ni)) with various molar ratios of Ru and Ni (*a*); dependences of $Q_{0.9}^{\mathrm{EtOH}(m)}$ *vs* Ru content and the ratio of weights of metals *m*(Ru)/*m*(Ru + Ni) in the composition of the Ru—NiO$_x$/C catalyst (*b*).

probable. The role of the promoting component (NiO$_x$) is the reoxidation of organic particles chemisorbed on ruthenium (see Scheme 2). This assumption agrees well with the results of chromatographic analysis of a mixture of products of ethanol electrooxidation on the catalysts Ru—NiO$_x$/C and Ru/C under conditions of stationary electrolysis.[6] According to these data, the yield of CO_2 on the binary system Ru—NiO$_x$/C is substantially higher than that on the monoruthenium catalyst.

Comparison of the adsorption data presented in Fig. 9 and in Table 1 with the results of studies of the kinetics of ethanol electrooxidation on the catalysts Ru—NiO$_x$/C of various compositions[24] shows that the highest value of $Q_{0.9}^{\mathrm{EtOH}(m)}$ referred to the weight of surface of ruthenium in the catalyst achieves a maximum when the catalyst oxidizes ethanol with the highest rate. The value of α*f* calculated from the time dependences of ethanol adsorption increases on going from Ru/C to Ru—NiO$_x$/C and Ru—VO$_x$/C (see Table 1). The highest energy heterogeneity (α*f* = 9) is characteristic of the catalyst with the largest amount of the nickel-containing components, $Ru_{37}Ni_{63}O_x$/C. The wide energy distribution of bonds formed upon adsorption in the system adsorbate—catalyst for the bimetallic systems is given by the results of measurements of the influence of the alcohol concentration on adsorption (Table 2).

According to the available data on the activity of the studied systems in the reaction of ethanol electrooxidation[5,6,24] on the monoruthenium catalyst in the region of low anodic polarizations (250—350 mV), the reaction is inhibited due to the surface covered with strongly bound products of ethanol chemisorption. Under these conditions, the metallooxide systems retain high activity due to the possibility of reoxidation of SCS involving the oxygen-containing components of the catalyst. Thus, there is certain agreement between the data on the kinetics and depth of ethanol oxidation and the parameters of adsorption curves for the systems studied. More uniform and, most likely, more strong ethanol adsorption on the catalyst

Table 1. Characteristics of the catalysts Ru (15 wt.%)/C, Ru—NiO$_x$/C (15 wt.% (Ru + Ni)), and $Ru_{60}V_{40}O_x$/C (20 wt.% (Ru + V)) according to the data of measurements of the kinetic curves of ethanol adsorption

Composition of catalyst Ru/Ni, wt.% (at.%)	α*f*	$Q_{0.9}^{\mathrm{EtOH}(m)}$ /mC (mg of Ru)$^{-1}$
100/0	5.6	280.0
75/25 (60/40)*	6.6	180.0
95/5 (92/8)	6.7	288.0
90/10 (84/16)	7.3	417.9
78/22 (68/32)	6.2	344.9
70/30 (58/42)	6.1	657.1
50/50 (37/63)	9.0	572.0

* Ru/V.

Table 2. Irregularity factors for the surface of the catalysts Ru (15 wt.%)/C, $Ru_{60}V_{40}O_x$/C (20 wt.% (Ru + V)), and $Ru_{68}Ni_{32}O_x$/C (15 wt.% (Ru + Ni)) according to the data of time and concentration measurements of adsorption

Catalyst	Time dependence, α*f*	Concentration dependence, *f*
Ru/C	5.6	5.4
$Ru_{60}V_{40}O_x$/C	6.6	6.6
$Ru_{68}Ni_{32}O_x$/C	6.2	6.9

Ru/C indirectly indicates that this catalyst is less efficient than the metallooxide systems characterized by a lower energy of bonding between adsorbed species and active sites of the catalyst.

Thus, specific features of ethanol adsorption in an alkaline electrolyte on the modified ruthenium catalyst were studied at various time intervals of adsorption, alcohol concentrations, and catalyst compositions. Analysis of the obtained dependences made it possible to compare the methods of estimation of surface coverages, one of which is based on a decrease in the amount of hydrogen adsorbed in the presence of alcohol, while the second method is based on the change in the quantity of electricity consumed for the oxidation of the adsorbate. It was shown that the latter better describes the characteristics of the considered catalytic systems. Similarity of the composition of the particles adsorbed on the catalytic systems during measurements was assumed on the basis of proximity of the adsorption parameters determined from the time and concentration measurements. It was found that the introduction of oxides into the composition of the ruthenium catalyst increased its energy heterogeneity and the value of maximum charge consumed for the oxidation of adsorbed organic particles. The metallooxide systems are characterized by the higher specific activity and extent of ethanol electrooxidation compared to those on the monoruthenium catalyst. Thus, the data on the kinetics and extent of ethanol oxidation agree with the results of adsorption measurements.

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