MECHANISM OF THE OXIDATION OF METHANOL ON A PLATINUM-RUTHENIUM ELECTRODE

V. S. Éntina and O. A. Petrii

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In [1-3] we studied some peculiarities of the behavior of a Pt + Ru electrode in solutions of methanol. The purpose of this communication was a more detailed study of the mechanism of the oxidation of methanol on an electrolytically mixed deposit (e.m.d.) of Pt and Ru (15% by weight Ru).

In the work we used the method of measuring the dependence of the current I on the time t at a constant electrode potential from the moment of its introduction into contact with methanol [4, 5]. The stationary polarization curves were measured both by galvanostatic and by potentiostatic methods. Both methods give coinciding results. For the potentiostatic measurements we used the P-5611 potentiostat of the Central Laboratory of Automation. The measurements were performed at 20 ± 2°C. The potentials φ_r are cited with respect to e.m.d. in the same solution.

We measured the I versus t curves for various φ_r (from 0.1 to 0.80 V) in acid and alkaline solutions of methanol of various concentrations c. By extrapolating the I versus t curves to t = 0 we found the values of the currents at the moment of introduction of the electrode into contact with the methanol solution. On the basis of the data obtained we constructed the log i versus φ_r curves presented in Fig. 1, in comparison with the data for a Pt/Pt electrode. To calculate the current density i, the true surface of the Pt + Ru electrodes was determined according to the length of the hydrogen portion of the charging curve in 1 N H_2SO_4 on the assumption that monolayer surface coverage with H_{ads} is observed at $\varphi_r = 0$. Two portions with different dependences of the rate of the process upon the potential are observed on the log i versus φ_r curves. In the hydrogen region, $(\partial \varphi_r/\partial \log i)_{pH,c} \simeq$ 70-80 mV in acid solutions and $\simeq$ 120 mV in alkaline solutions. In the potential region 300-600 mV, the rate of the process depends little upon the electrode potential: $(\partial \varphi_r/\partial \log i)_{pH,c} \simeq$ 700-750 mV. For the oxidation of methanol on a

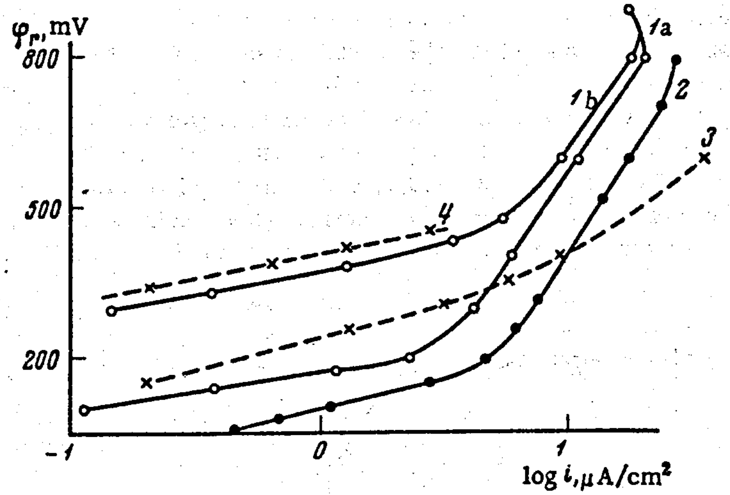

Fig. 1. Dependence of the rate of electrooxidation of methanol on the potential in 1 N H_2SO_4 (1, 3, 4) and 1 N KOH (2) in the first moment after the substance is placed in contact with Pt + Ru (1a, 2) and Pt/Pt (3) electrodes and under stationary conditions (1b) on a Pt + Ru electrode (c_{CH_3OH} = 0.1 M); 4) polarization curve of the electrooxidation of the chemisorption product of methanol on a Pt + Ru electrode.

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surface of a Pt + Ru electrode free of chemisorption products, just as in the case of a Pt/Pt electrode [4, 5], a low dependence upon the pH of the solution is characteristic. The currents measured in 1 N H_2SO_4 and 1 N KOH practically coincide. The current of the oxidation of methanol at the first moment of time on a Pt + Ru electrode, independent of the potential, is proportional to the volume concentration of methanol: $(\partial \log i/\partial \log c)_{\varphi_r,\mathrm{pH}} \simeq 1$ (Fig. 2). The data obtained can be explained if we assume that on a Pt + Ru electrode, just as on Pt/Pt, the oxidation of methanol at the first moment of time is determined by a reaction of dehydrogenation and consider the change in the surface coverage by adsorbed hydrogen with changing electrode potential [5].

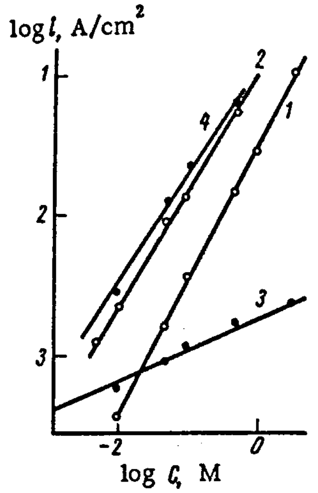

Fig. 2. Dependence of the rate of oxidation of methanol on the concentration on a Pt + Ru electrode at the first moment after introduction: 1) $\varphi_r = 200$ mV; 2) $\varphi_r = 450$ mV, and under stationary conditions: 3) $\varphi_r = 350$ mV; 4) $\varphi_r = 600$ mV.

A comparison of the currents of the dehydrogenation of methanol on Pt+Ru and platinum electrodes (Fig. 1) shows that at potentials of the hydrogen region the reaction proceeds with an appreciably higher rate on the mixed catalyst, whereas at φ_r of the "double layer" region, platinum is more active in the dehydrogenation reaction. Such a nature of the dependence may be due to the superposition of two effects: acceleration of the dehydrogenation reaction in the transition to a Pt + Ru electrode and earlier appearance of adsorbed oxygen on the surface of the electrode, inhibiting the process. The higher value of the slope of the polarization curve in the case of a Pt + Ru electrode in comparison with Pt/Pt at φ_r 300-600 mV (~700-800 mV instead of ~400 mV) evidently also can be explained by superposition of the inhibiting effect of the adsorbed oxygen. On the basis of the data obtained, we can understand the apparent contradiction between the conclusion of high activity of Pt + Ru alloys in the reaction of deuteroexchange between methane and deuterium in the gas phase [6] and the low activity of these alloys in the process of electrooxidation of methane, which is determined by the reaction of dehydrogenation [7]. In the first case the reaction proceeds on a reduced surface of the catalyst, while in the second the investigation was conducted at φ_r = 300-600 mV, i.e., in the presence of adsorbed oxygen on the surface.

For a study of the dependence of the adsorption of methanol upon φ_r, at the φ selected, maintained by a potentiostat, the electrode was brought into contact with methanol and exposed until the establishment of the stationary state, after which φ_r was abruptly lowered to 30 mV, and washing was performed. From the anodic charging curve then obtained, we determined the amount of the chemisorbed substance. To characterize the value of the adsorption θ, we used the ratio of the amount of chemisorbed substance to the amount of hydrogen adsorbed in the background solution at $\varphi_r = 0$; moreover, θ was set equal to 1 at the maximum value of the indicated ratio. The two quantities were expressed in electrical units. The dependence found is presented in Fig. 3. The region of maximum adsorption on a Pt + Ru electrode lies at φ_r = 0.2-0.35 V. The drop in the region of φ_r > 0.35 V is evidently due to the oxidation of chemisorbed particles, which occurs at an appreciable rate [4]. Since the overvoltage of the oxidation of methanol under standard conditions on a Pt + Ru electrode is ~150 mV lower than on Pt/Pt,

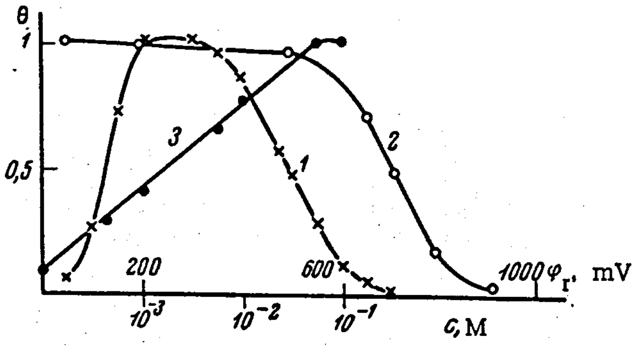

Fig. 3. Dependence of the surface coverage of Pt + Ru (1) and Pt/Pt (2) electrodes on the potential in a solution of 0.05 M CH_3OH + 1 N H_2SO_4 and dependence of the adsorption of methanol on the Pt + Ru alloy upon c_{CH_3OH} at φ_r = 200 mV (3).

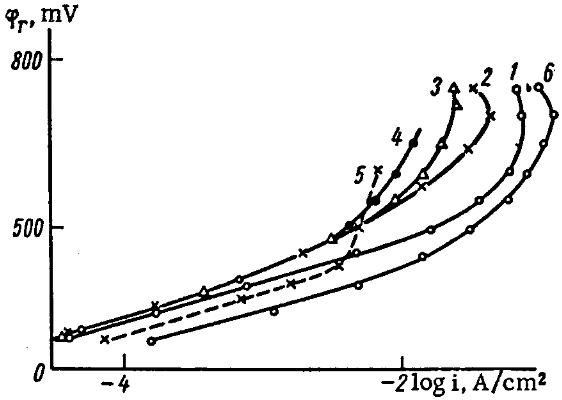

Fig. 4. Stationary polarization curves of the oxidation of 3 M CH_3OH on a Pt + Ru electrode in solutions with pH: 1) 0.3; 2) 1; 3) 1.8; 4) 2.3; 5) 12.4; 6) 13.6. The points given are calculated on the basis of the visible surface.

the descending branch of the θ versus φ_r curve also is shifted by ~150 mV in the cathodic direction in comparison with a Pt/Pt electrode. The decrease in the adsorption of methanol as $\varphi_r = 0$ is approached is due to a decrease in the rate of dehydrogenation of alcohol with increasing adsorption of hydrogen, as well as the hydrogenation of methanol, possible at low φ_r [2].

Figure 3 presents the dependence of the adsorption of methanol on a Pt + Ru alloy at φ_r of maximum coverage upon c. In the region of c from $5 \cdot 10^{-4}$ to $5 \cdot 10^{-2}$ M, θ is proportional to log c, i.e., the Temkin isotherm is formally obeyed:

$$\theta = \text{const} + \frac{1}{f} \ln c,$$

where f is the surface inhomogeneity factor. An analogous dependence has been observed for the adsorption of methanol [8, 9] and aliphatic alcohols on a smooth platinum electrode [10]. The inhomogeneity factor f, according to Fig. 3, is equal to ~7 on a Pt + Ru electrode. However, from the standpoint of the data of [3] on the irreversible nature of the adsorption of methanol on the electrode, the question of the treatment of the θ versus log c dependence is in dispute [11]. It may be assumed that the observed dependence represents the "stationary" adsorption isotherm and reflects the establishment of equilibrium between the process of adsorption of methanol with the formation of HCO [3] and oxidation of HCO particles to CO_2 at high φ_r or between the process of dissociative adsorption of methanol and the hydrogenation of methanol to methane at low φ_r.

The measurements of the stationary polarization curves were conducted in solutions of 1 N (H_2SO_4 + Na_2SO_4) and 1 N (NaOH + Na_2SO_4) with the following pH values: 0.3; 1; 1.8; 2.3; 12.4; 13.6 (Fig. 4). In acid solutions at low φ_r, the change in pH has practically no effect upon the reaction rate. In the region $\varphi_r > 450$ mV, with increasing pH, earlier passivation of the process is observed. In alkaline solutions, especially in the transition to highly alkaline pH, the reaction rate increases somewhat; however, on the whole, the effect is small in comparison with the data for Pt/Pt [5]. Independent of the pH at low φ_r, $(\partial \varphi_r/\partial \log i)_c \simeq 60$-65 mV. The polarization curves of the electrooxidation of methanol passed through a maximum at 600-800 mV, after which a drop in the current is observed (Fig. 4). In the region of φ_r ~200-400 mV, the rate of the process depends little upon the methanol concentration, $i = kc^{0.2}$ (Fig. 2). The dependence upon the concentration increases with increasing φ_r, and at $\varphi_r = 600$ mV, $(\partial \log i/\partial \log c)_{\varphi_r,\, pH} = 0.75$.

The experimental data obtained permit us to assume that on a Pt + Ru electrode, both in acid and in alkaline solutions, the step determining the rate of the process under stationary conditions is the interaction of chemisorbed particles with particles of OH_{ads} according to the scheme proposed earlier for a Pt/Pt electrode:

$$H_2O - e^- \rightleftarrows OH_{ads} + H^+ \quad \text{(acid solutions)}$$

$$OH^- - e^- \rightleftarrows OH_{ads} \quad \text{(alkaline solutions)}$$

$$OH_{ads} + RH_{ads} \xrightarrow{\text{slow}} R\cdot + H_2O.$$

The kinetic equations corresponding to such a scheme [5], at $[RH]_{ads}$ = const, are approximately fulfilled at low φ_r. As a confirmation of this, the overvoltage of the oxidation of firmly chemisorbed methanol and the process in the presence of methanol in solution differ by only ~25 mV (Fig. 1). When φ_r is increased, the surface coverage $[RH]_{ads}$ decreases (Fig. 3), which leads to a deviation of the shape of the polarization curve from linear, and at sufficient φ_r, the rate of adsorption of methanol begins to exert an appreciable influence upon the reaction rate. As a result of this, the dependence of the rate of the process upon the concentration of the organic substance increases. At still more anodic φ_r, the process is inhibited as a result of the adsorption of oxygen [12]. The acceleration of the process in alkaline solutions may be associated with a change in the nature of the reacting particle in strongly alkaline solutions [12, 5].

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