NATURE OF THE CHEMISORPTION PRODUCTS OF METHANOL ON THE SURFACE OF A Pt + Ru ELECTRODE

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Many recent reports [1-8] deal with the nature of the chemisorption products of organic compounds on the surface of platinized and smooth platinum electrodes. The authors of [1, 2] have shown that under certain conditions particles of overall composition HCO are adsorbed on a Pt/Pt electrode from methanol solutions. It seemed of interest to study the products chemisorbed from methanol solutions in the case of a Pt + Ru catalyst. Platinum – ruthenium alloys are of interest because the electrooxidation of methanol is much faster on them than on Pt/Pt electrodes [9, 10].

The method used for the galvanostatic measurements is described in [1, 22]. We used a TsLA P-5611 potentiostat for the potentiostatic measurements. Electrolytically mixed deposits of Pt and Ru (15 wt.% Ru) were deposited on a platinum plate with visible surface 2 cm^2 by the method in [9, 12]. Before an experiment the electrodes were cathodically polarized in 0.1 N H_2SO_4 at current density ~ 10 mA/cm^2. All the measurements were performed at room temperature. The potentials φ_r are related to a reversible hydrogen electrode in 0.1 N H_2SO_4.

The electrode, stabilized at the selected value of φ_r^0 with an open circuit, was brought into contact with the methanol solutions and the potential displacement curves measured. With increasing methanol concentration the rate of potential displacement increases and the value of the steady potential φ'_r decreases (Table 1). At constant methanol concentration, the lower the initial potential φ_r^0 the smaller will be the ultimate potential. These data agree with previous data [1, 2] on the adsorption of methanol on a Pt/Pt electrode. After removal of methanol from the electrodes the charging curve displays two plateaux, one of which Q_1 is due to ionization of adsorbed hydrogen, the other Q_M to oxidation of the chemisorbed substance (Fig. 1).

The most striking fact revealed by a comparison of these curves and the analogous curves for a Pt/Pt electrode [1, 2] is that Q_1 is less than Q_M in dilute methanol solutions and with φ_r^0 greater than 300 mV. This is understandable if we bear in mind that in the φ_r^0 range from 300 to 700 mV the capacitance of a Pt + Ru electrode is much greater than that of a Pt/Pt electrode. In consequence , on a Pt + Ru electrode a considerable part of the hydrogen formed during dehydrogenation of methanol goes on the charging of the electrode. The high capacitance of a Pt + Ru electrode at φ_r 300-700 mV is evidently due to the fact that with Ru in the deposit the oxidation of the surface takes place earlier [9]. The amount of hydrogen Q_2 ionized (or reacted with the absorbed hydrogen) can be approximately calculated from the charging curve in the base electrolyte (Fig. 1) if we assume that with φ_r in the range 300-700 mV the charging curve is not greatly changed by addition of methanol to the solution. Allowing for Q_2, the amount of hydrogen Q_H, chemisorbed during dehydrogenation of methanol, and the amount of chemisorbed substance Q_M, expressed in electrical units, are approximately equal (Table 1).

With φ_r^0 = 300 mV, virtually all the hydrogen formed during dehydrogenation of methanol remains on the electrode's surface because the initial potential corresponds to the potentials of the beginning of the hydrogen sector. With φ_r^0 = 300 mV the values of Q_H and Q_1 (Fig. 2) are similar in both acid and alkaline solutions.

From the equality of the amount of chemisorbed substance and of adsorbed hydrogen, we can infer that, as in the case of platinized platinum [1, 2] particles of overall composition HCO are adsorbed on a Pt + Ru electrode. The fact that the ratio Q_H/Q_M is constant (about 1) indicates that hydrogenation of the initial molecules and the electrooxidation of the chemisorbed substance to CO_2, which occur on a Pt + Ru alloy [13], do not have a marked effect on the ratio of the chemisorption products in methanol solutions of these concentrations.

Out conclusions regarding the nature of the chemisorption products on a Pt + Ru electrode were confirmed by another method, previously used [4, 5] for studying the adsorption of methanol and formic acid on a smooth Pt electrode. The electrode, kept potentiostatically at constant potential, was brought into contact with the methanol

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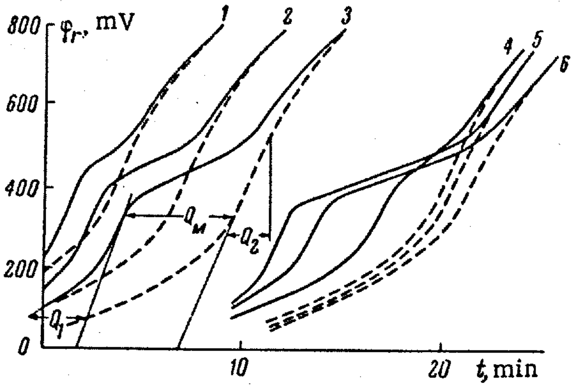

Fig. 1. Electrooxidation curves of substances chemisorbed in methanol solutions of different concentrations: 1) 10^{-3}, 2) 10^{-2}, 3) 10^{-1}, 4, 5, 6) $5 \cdot 10^{-1}$ M. Initial potential φ_r^0: 1, 2, 3) 500, 4) 60, 5) 500, 6) 900 mV. The dashed lines are the charging curves in background electrolyte 1 N H_2SO_4 ($i = 3 \cdot 10^{-4}$ amp/cm^2).

TABLE 1. Rate of φ_r' Versus Time (background electrolyte–1 N H_2SO_4)

$[CH_3OH]$, mole/liter	φ_r^0, mV	φ_r', mV	Δt, min	Q_H, C	Q_M, C
10^{-3}	500	202	100	0,075	0,069
10^{-2}	500	130	60	0,119	0,136
10^{-1}	500	88	60	0,191	0,201
$5 \cdot 10^{-1}$	500	65	40	0,223	0,237

TABLE 2. Values of $Q_H - \Delta Q_H$

Background electrolyte*	Q_H	ΔQ_H	$Q_H - \Delta Q_H$	Q_H
1 N H_2SO_4	1,07	0,15	0,92	0,89
1 N NaOH	0,31	0,03	0,28	0,27

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* The experiments in acid and alkali were performed on electrodes with different true surfaces.

solution and the time dependence of the current flowing through the cell was plotted (Fig. 3a). The dehydrogenation current decreases with time, owing to accumulation of the chemisorption products on the electrode, and approaches the steady current of the electrooxidation of methanol. At the measurement potential (200 mV) the steady rates of methanol oxidation are similar to the background-electrolyte current. By integrating the (I, t) curve, we find the amount of adsorbed hydrogen ionized during adsorption of methanol on the electrode's surface. The potential was then reduced suddenly to 30 mV and, after removal of methanol from the electrode, the charging curve was plotted (Fig. 3b). The amount of chemisorbed product was determined from the break on the charging curve.

Preliminary experiments were performed to determine the influence of gaseous hydrogen and cathodic polarization on the chemisorbed substance. For this purpose, after removal of methanol from the electrode hydrogen was passed through the solution or, alternatively, the electrode was cathodically polarized at current density ~5 mA/cm^2. It was found that neither hydrogen nor cathodic polarization have any influence on the amount of chemisorbed product obtained. From this and the low adsorption of methanol at φ_r close to 0 (Fig. 1), we can assume that the amount of substance adsorbed on the electrode at 200 mV is practically unchanged by changes of up to 30 mV in the electrode potential.

From a comparison of the charging curve of Pt + Ru (CH_3OH_{ads}) and the charging curve in the background electrolyte (Fig. 3), it follows that in the presence of an organic substance the amount of hydrogen adsorbed on the electrode at potentials more positive than that at which methanol is added falls markedly: $\Delta Q_H = l_1 - l_2$. This is an indication that part of the hydrogen adsorbed on the electrode at the addition potential of methanol is displaced

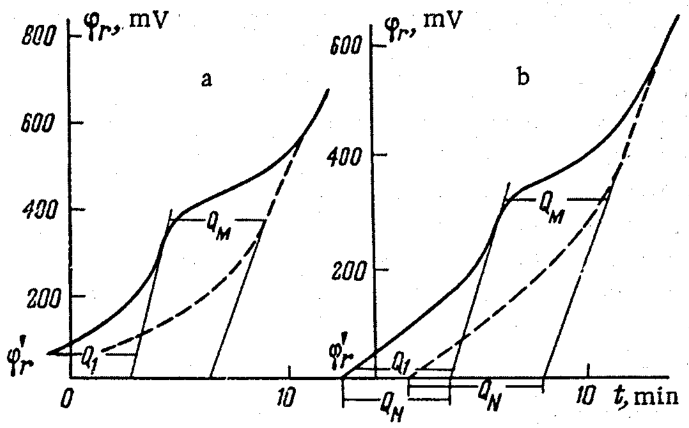

Fig. 2. Charging curves after removal of methanol, from a Pt + Ru electrode in 1 N H_2SO_4 (a) and 1 N NaOH (b); φ_r^0 = 300 mV CH_3OH = 0.5. The dashed lines are background-electrolyte charging curves. Current densities: a) $3 \cdot 10^{-4}$ A/cm²; b) $5 \cdot 10^{-4}$ A/cm².

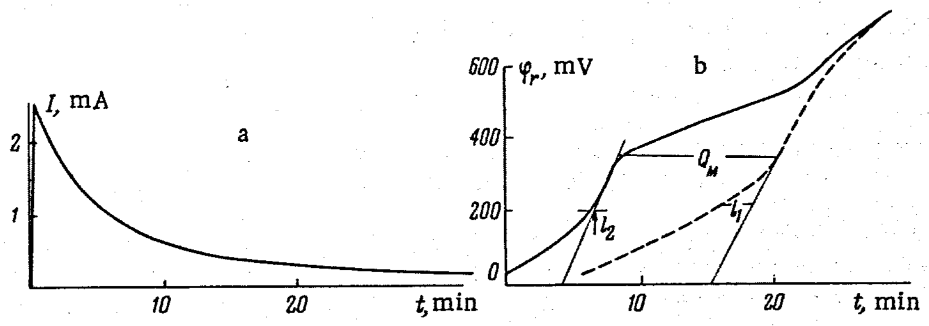

Fig. 3. a) Rate of oxidation of methanol, plotted versus time when a Pt + Ru electrode is brought into contact with 0.05 M CH_3OH = 1 N H_2SO_4 at φ_r^0 = 200 mV; b) electrooxidation curve of substances chemisorbed on a Pt + Ru electrode at 200 mV in 0.05 M CH_3OH + 1 N H_2SO_4 ($i = 5.5 \cdot 10^{-4}$ A/cm²). The dashed line is the charging curve in the background electrolyte.

by the chemisorption product of methanol and ionized. Therefore to determine the amount of hydrogen formed by dehydrogenation we must subtract from the value of Q_H, found by integrating the (I, t) curve, the amount of hydrogen ΔQ_H displaced by the chemisorbed product. The results are given in Table 2 and confirm that we have drawn a correct conclusion regarding the adsorption of HCO particles on the surface of Pt + Ru electrodes.

If we linearly extrapolate the initial section of the charging curve of Pt + Ru $(CH_3OH)_{ads}$ to $\varphi_r = 0$, we see (Fig. 2) that the total amount of adsorbed hydrogen, Q_H', plus chemisorbed substance, Q_M, is 25-30% greater than the amount of hydrogen adsorbed at $\varphi_r = 0$ in the base electrolyte solution (Q_H^0). In the case of a Pt/Pt electrode [1, 2], ($Q_H' + Q_M$) is equal to Q_H^0. Two explanation can be given for the result obtained on a Pt + Ru electrode: a) part of the adsorbed particles occupies three hydrogen sites, and the other part two hydrogen sites (surface atoms of the alloy); b) with $\varphi_r = 0$ the surface of the Pt + Ru alloy is not completely covered by hydrogen, while the organic substance can occupy centers on which hydrogen is not adsorbed with $\varphi_r = 0$. Further experimental work is necessary before we can decide which of these explanations is correct.

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