BEHAVIOR OF A PLATINUM-RUTHENIUM ELECTRODE IN SOLUTIONS OF SATURATED ALCOHOLS AND ACETALDEHYDE

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The ability of methanol to be hydrogenated in the region $\varphi_r > 0$ at room temperature on a Pt + Ru electrode was demonstrated. The evolution of hydrogen in alkaline solutions of methanol at potentials more anodic than the reversible hydrogen potential was detected and discussed. When a Pt + Ru electrode is introduced into solutions of C_2H_5OH, n-C_3H_7OH, CH_3CHO, dehydrogenation and destructive hydrogenation processes occur. The Pt + Ru electrode is a more active catalyst in reactions of dehydrogenation and hydrogenation of saturated alcohols and acetaldehyde than is Pt/Ru. Just as in the case of Pt/Pt, a "degasified" surface of a Pt + Ru catalyst exerts a stronger destructive effect upon alcohols than a surface coated with hydrogen.

Recently the behavior of a Pt/Pt electrode in solutions of saturated alcohols, aldehydes, and acids has been investigated in detail in a number of studies [1, 2]. It has been shown that the summary process, which occurs when platinized platinum is in contact with solutions of alcohols and aldehydes containing more than one carbon atom, is made up of reactions of dehydrogenation, hydrogenation, and self-hydrogenation of the starting materials and the products of their decomposition (chiefly at the C_1-C_2 bond). An analogous study of the reactions of simple organic compounds on other platinum metals is also of interest.

In this work we investigated the behavior of a platinum-ruthenium (Pt + Ru) electrode in solutions of saturated alcohols and aldehydes. The selection of this catalyst was determined by the fact that, as was shown earlier [3, 4], the rate of electrooxidation of methanol on it exceeds the rate of the process of platinum by almost three orders of magnitude. According to the literature data [4, 5], we might have expected an acceleration of other reactions of organic compounds as well as a mixed catalyst.

The measurement procedure was described in [6]. In the work we used electrolytically mixed deposits (e.m.d.) of platinum and ruthenium, produced according to the method of [3], and skeletal platinum-ruthenium catalysts. The latter were prepared by fusion of a mixture of platinum, ruthenium, and aluminum powders in an atmosphere of hydrogen at 800°. The alloys corresponded to the composition Me_2Al_3. To remove the aluminum, the ingot obtained in the fusion was exposed for a long period in a concentrated solution of alkali, then heated in 1N H_2SO_4; the electrode potential was maintained within the range 400-600mV. The values of the potential φ_r in the work are given with respect to the reversible hydrogen electrode in the same solution. The electrode thus treated was wrapped in an individual platinum grid and used for the measurements. Before the experiment, the electrodes were subjected to anodic, and then cathodic polarization in a separate vessel at a current density of 10-20 mA/cm^2 of visible surface or per 10 mg of catalyst.

In Fig. 1 the charging curves of Raney and electrolytically deposited electrodes, containing 10% ruthenium, in 1N H_2SO_4 are compared. The shape of the charging curves is analogous in both cases, and the observed differences are small. We tested skeletal catalysts containing 5, 10, and 20% ruthenium. A criterion of the activity of the catalysts was the rate of oxidation of methanol under nonstationary and stationary conditions. Both the curves of the shift of the potential after the introduction of methanol and the polarization curves of the electrooxidation of methanol under stationary conditions for skeletal electrodes containing 10 and 20% ruthenium are close (Fig. 2). In a comparison of the polarization curves on different catalysts, in view of the absence of data on the values of their true surfaces, current densities at which the charging curves of the electrodes coincided in duration were taken as identical. When the current densities are calculated in this way, the polarization curves on different catalysts at low φ_r differ little from the corresponding curves on e.m.d. of platinum and ruthenium. However, the slopes of the

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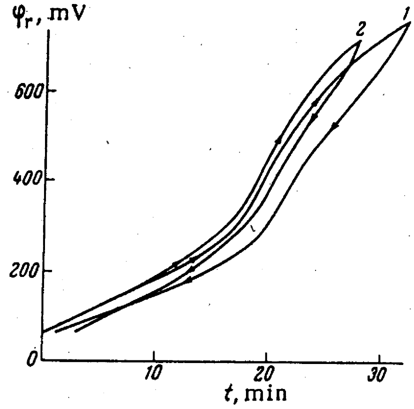

Fig. 1. Charging curves of electrolytically deposited (1) and Raney (2) platinum ruthenium electrodes at [Pt]:[Ru] = 9:1 in 1N H_2SO_4; $i = 10^{-4}$ A/cm^2 (1); $I = 4.5 \cdot 10^{-3}$ A (2).

curves on porous skeletal electrodes comprise ~90 mV, whereas on e.m.d. they are ~50 mV. When the current density is increased above the value indicated in Fig. 2, a sharp increase in the polarization of the skeletal electrodes is observed.

Experiments on the collection of gaseous reaction products of organic compounds were conducted on a skeletal catalyst containing 15% ruthenium. The background was 1N H_2SO_4 or 1N NaOH. All the experiments were conducted at room temperature, 20 ±2°C. The gases were analyzed chromatographically. The hydrocarbons were separated on a column with brand ASM silica gel. A parallel analysis of the gas with separation on 13X molecular sieves was conducted for the determination of hydrogen.

When a Pt + Ru electrode is introduced into a solution of CH_3OH, its potential is shifted in the negative direction [3]; in alkali lower values of φ_r' are reached than in acid. Thus, after the introduction of 3M CH_3OH at ~500 mV into alkaline solutions, after 2 h, a value of −1-2 mV is established, while in acid solutions it is 25-30 mV. At φ_r^0 = 60 mV, after 1 h, −2 mV is reached in alkali, and −0.7 mV in acid. It should be mentioned that although lower final values of the potentials are established on a Raney catalyst than on an e.m.d. of Pt and Ru, the rates of displacement of φ_r are lower during the first period after introduction of the organic substance, which is evidently due to the difficulty of delivery of the reacting substance to the surface of the skeletal electrode, which possesses high porosity.

In contrast to the Pt/Pt electrode, on an alloy of Pt + Ru, both Raney and electrolytically deposited, after it is brought into contact with methanol, an evolution of gaseous products is observed. The first gas bubbles appear after φ_r ~30 mV is reached by the electrode. According to semiquantitative chromatographic analysis, the gas liberated in alkaline solutions is hydrogen and contains only traces of methane.[*] In the case of acid solutions in the gas phase, in addition to hydrogen (92%), there are substantial amounts of methane (up to 7%) and about 1% CO_2. The evolution of methane is an indication of the ability of methanol to be hydrogenated at a rather high rate in the region $\varphi_r > 0$ at room temperature. On a Pt/Pt electrode, according to the data of V. F. Stepin, hydrogenation of methanol in acid solutions occurs only at increased temperatures (~80°). CO_2 was detected in the gas phase after the introduction of methanol, both at +500 mV and at +60 mV, which is an indication of profound oxidation of the methanol molecules, not only on the degasified surface of the Pt + Ru electrode, but also on the surface coated with adsorbed hydrogen.

In the case of a Pt/Pt electrode, the amount of the chemisorbed substance in methanol solutions at low φ_r^0 approaches zero, while at φ_r^0 close to zero, methanol is not dehydrogenated at an appreciable rate. The result obtained on a Pt + Ru electrode in concentrated solutions of methanol shows that in this case the method of determining the nature of chemisorbed particles used in the case of the Pt/Pt electrode in [7] and based upon the assumption of dehydrogenation of the molecules with an opened chain only to the chemisorption products cannot be used.

The evolution of hydrogen when methanol in alkaline solutions comes in contact with the surface of a Pt + Ru catalyst, which occurs at potentials more anodic than the reversible hydrogen potential, is of special interest. We are evidently the first to have noted this phenomenon in the case of methanol, although it has been observed heretofore for a number of other organic substances on various catalysts [2, 8]. As will be shown below, the determination of the causes of the evolution of hydrogen at the anodic potentials in alkaline solutions of methanol and the causes of the absence of this process in the case of contact of other organic compounds with Pt + Ru electrodes, will require further experimental investigation.

This phenomenon may be explained by chemical interaction of the products formed in the contact of methanol with the surface of Pt + Ru electrode among themselves, with water molecules, or with substances adsorbed on the electrode. Such a representation, as applied to the process of evolution of hydrogen at the anodic potentials in solutions of formic acid on a Pt/Pt electrode, was discussed earlier in [2]. Evidently in methanol solutions the

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[*] All the analyzed samples also contained argon, which was used to free the solutions from oxygen. Argon was not taken into consideration in the calculation of the gas composition in this work.

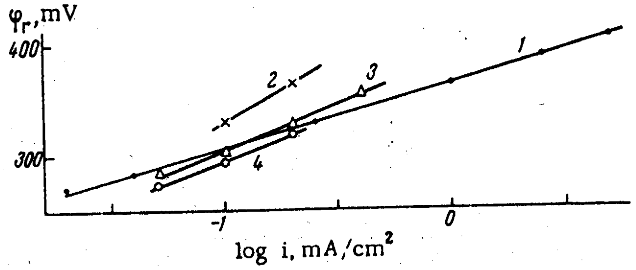

Fig. 2. Stationary polarization curves of the electrooxidation of methanol (0.5 M) in 1N H_2SO_4 on e.m.d. of platinum and ruthenium (1) ([Pt]:[Ru] = 9:1) and Raney Pt + Ru electrodes, with ruthenium contents: 2) 5; 3) 10, 4) 20%.

Substance	Background	φ_r^0, mV	Δt, h	φ_r^1, mV	Data of analysis,* vol. %			
					H_2	CH_4	C_2H_6	C_3H_8
3M CH_3OH	1 N H_2SO_4	60	16		10	90	—	—
3 M C_2H_5OH	1 N H_2SO_4	504	16	50,5	—	92	8	—
	1 N NaOH	500	2	36	3	96	1	—
	1 N H_2SO_4	60	2,5	28	8	55	37	—
	1 N NaOH	60	1,5	7,1	9	90	traces	—
3 M C_3H_7OH	1 N H_2SO_4	400	0,75	75,7	—	35	50	15
	1 N NaOH	500	12	33	—	31	68	traces
	1 N H_2SO_4	60	0,75	34,9	—	30	40	30
	1 N NaOH	60	1,5	7,8	—	11	83	traces
3 M CH_3CHO	1 N H_2SO_4	500	3,5	187,4	—	95	5	—
		60	12	188	—	89	11	—

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* No analysis of the gases for butane was performed.

evolution of hydrogen becomes possible as a result of the rapid rates of process of oxidation on a Pt + Ru catalyst and the consequent appearance of substantial amounts of intermediate oxidation products in the layer near the electrode.

After ethanol and propanol are brought into contact with a Pt + Ru electrode, both at 260 mV and at 500 mV, the electrode potential is shifted only in the negative direction, and a vigorous evolution of gas bubbles is observed. The evolution of gaseous products is more intensive than under analogous conditions on platinum [2]. In alkaline solutions, φ_r is shifted at a greater rate, and the established values of φ_r' are lower than in acid solutions. The results of an analysis of the gases liberated after the introduction of ethanol and propanol at various φ_r are cited in the table.

The gases liberated in solutions of ethanol and propanol are products of processes of destructive hydrogenation. After the introduction of ethanol at 60 mV, the gas phase contains appreciable amounts of hydrogen, whereas only traces of hydrogen are detected after the introduction of the substance at 500 mV, which is evidently due to the establishment of higher values of φ_r' in the second case. In the case of contact of the alcohols with the surface of the Pt + Ru electrode, there is both hydrogenation of the C–O bond and a substantial degree of cleavage of the molecules at the C_1-C_2 bonds. As a result of this reaction, the gas phase is rich in a hydrocarbon containing one carbon atom less than the initial alcohol. On a Pt + Ru catalyst, the decomposition of the molecule is so pronounced that the hydrocarbon with a smaller number of carbon atoms predominates in the gas phase, in contrast to a Pt/Pt electrode [2].

In the hydrogenation of propanol on a Pt + Ru catalyst, the gas phase contains from 10 to 30% methane; on Pt/Pt, methane was not detected in appreciable amounts [2]. Evidently the appearance of methane is due to noticeable decomposition of the propanol molecules at the C_2-C_2 bond. As is shown by the results of analysis, hydrogenation of alcohols at the C–O bond in alkaline solutions is negligible, and the gas phase contains only traces of a hydrocarbon with the same number of carbon atoms as the initial alcohol. Just as in the case of a Pt/Pt electrode [2], a "degasified surface" of a Pt + Ru catalyst exerts a stronger destructive effect upon the alochols than a surface coated with adsorbed hydrogen.

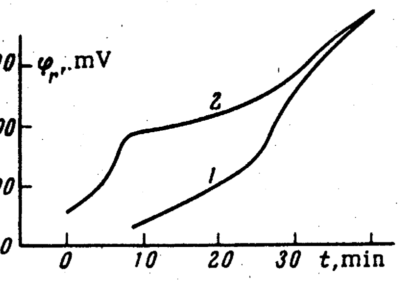

Fig. 3. Charging curve after washing of a Pt-Ru electrode to remove ethanol (2); (1) charging curve in the background solution of 1N H_2SO_4; $c(C_2H_5OH) = 0.5$ M, $i = 10^{-4}$ A/cm^2. Potential of introduction of ethanol 0.4 V.

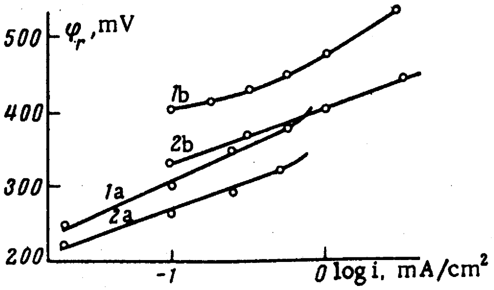

Fig. 4. Polarization curves of the electrooxidation of ethanol under stationary conditions on Pt/Pt (1) and Pt + Ru (9:1) (2) electrodes in 1N H_2SO_4 (a) and 1N NaOH (b).

Independent of the concentration of the substances and φ_r^0, after the alcohols are brought into contact with a Pt + Ru electrode, there is a shift in the potential only in the negative direction, and values of φ_r, close to the reversible hydrogen potential are reached. This result, with the simultaneous intensive evolution of reduction products of alcohols, is evidence that the rate of dehydrogenation of organic substances is rather high in the case of low anionic potentials, and it exceeds the rate of their reduction by adsorbed hydrogen. Even after substantial time intervals, no equilibrium between the indicated processes is established. Thus, 2 h after the introduction of the alcohols, the rate of change of the potential is ~2 mV/min, while after 12 h, φ_r still continues to be shifted in the negative direction. In this respect the Pt + Ru electrode also differs from the Pt/Pt electrode, on which the nature of the curves of the shift in the potential is determined by the initial φ_r^0 and by the alcohol concentration [1, 9], and after short periods of time, a practically stationary value of φ_r, is established.

After the Pt + Ru electrode is washed free of organic substances, hydrogen and chemisorption products are detected on the surface (Fig. 3). The amount of hydrogen, however, is approximately 1.5-2 times smaller than under analogous conditions in solutions of methanol, while the complete oxidation of the chemisorbed substances ends at more anodic potentials in comparison with the oxidation potentials of chemisorbed methanol.

After acetaldehyde was brought into contact with a Pt + Ru electrode at φ_r^0 close to zero, the potential was shifted in the positive direction, and there was a vigorous evolution of gas, which is the product of destructive hydrogenation of acetaldehyde by adsorbed hydrogen (the table). In the case of a "degasified" surface, after an original shift of the potential in the negative direction to ~172 mV, it is shifted in the direction of more positive values, i.e., just as on a Pt/Pt electrode, a minimum is observed, on the curve of the shift of φ_r. The gaseous products liberated in this case contain only half as much ethane as in the first case. The final potentials established are approximately the same, independent of φ_r^0.

The results of a measurement of the stationary polarization curves of the electrooxidation of ethanol on a Pt–Ru electrode are presented in Fig. 4. In the polarization of a Pt + Ru electrode in ethanol solutions, a stationary state is established very slowly, which is also characteristic of measurements of a Pt/Pt electrode. The slope of the polarization curves is ~95 mV. Oxidation of alcohol proceeds at higher rates in alkaline solutions than in acid solutions, although the differences is substantially smaller in comparison with a Pt/Pt electrode. A comparison of the polarization curves shows that on a mixed Pt + Ru catalyst, the rate of electrooxidation of ethanol is higher than on platinum, but the effect is not so great as for the electrooxidation of methanol.

From the data obtained, it follows that a Pt + Ru electrode is a more active catalyst in reactions of dehydrogenation and hydrogenation of saturated alcohols and acetaldehyde and exerts a stronger destructive effect upon organic substances than a Pt/Pt electrode. A comparison of the results of measurements of the stationary polarization curves of the electrooxidation of methanol, ethanol, and formic acid [10] with data for a platinum electrode shows that the acceleration of the process on a mixed catalyst is most pronounced for the oxidation of methanol.

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