ELECTROOXIDATION OF METHANOL ON Pt + Ru AND Ru ELECTRODES AT DIFFERENT TEMPERATURES

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UDC 541.135.52-44

We studied the effect of temperature on electrooxidation of methanol under stationary conditions on an Ru electrode and Pt + Ru electrolytically mixed deposits (emd) containing 10, 25, or 40 wt.% ruthenium. These measurements are of interest, particularly for determining the optimum composition of a Pt + Ru catalyst in oxidation of methanol at different temperatures and for elucidating the problem of the high catalytic activity of a porous Ru electrode at higher temperatures with respect to this reaction [1]. For subsequent elucidation of the mechanism of CH_3OH oxidation on a Pt + Ru electrode, we analyzed the oxidation products under stationary conditions on HCHO and HCOOH. The results were compared with data for a Pt/Pt electrode. Formaldehyde was determined by the color reaction with chromotropic acid [3], and formic acid by iodimetric titration [4].*

The stationary polarization curves were measured by the galvanostatic method. The electrodes were made by the method in [5-7]. Before an experiment they were cathodically polarized in H_2SO_4. We found that in the case of prolonged anode polarization of the emd at oxygen liberation potentials the shapes of the charging curves gradually approached those of a Pt/Pt electrode. Analysis of the electrolyte showed that this was due to slow solution of ruthenium from the deposit, which was possibly bounded only by the surface layer. The discrepancy between these results and those in [7] is apparently due to the fact that our previous method [7] was insufficiently accurate to record solution of ruthenium from several surface monolayers when the deposits were more than 100 monolayers thick. The current density i was calculated per 1 cm^2 of true surface. The latter was determined from the length of the charging curve in 1 N H_2SO_4 with φ† = 0 to 200 mV for Ru and 400 mV for emd, on the assumption that, with Ru = 0, an H atom is adsorbed on each surface atom of the catalyst. Such a calculation for a Pt + Ru electrode (10% Ru) gives values agreeing with those obtained by the BET method for low-temperature adsorption of nitrogen.‡ The surface area of an Ru electrode changes by only ∼10% when heated to 80°C. In the case of emd an increase in temperature leads to recrystallization and halving of the surface area. Recrystallization is also observed to a lesser extent at 20°C.

The reader will see from Fig. 1 that with an increase in temperature from 22 to 72°C the oxidation overvoltage of methanol on Ru becomes less than on Pt/Pt in a wide range of i values. However, under these conditions at higher φ_r we observe a marked increase in the slope of the (log i, φ_r curve). The activation energy E_a, calculated for φ_r = 520 mV, is ∼11.kcal/mole. The data can be explained if we assume that on Ru at 20°C the slow stage of oxidation is chemisorption of methanol. This is supported by data on the curves of φ_r displacement after making contact with the methanol solution [6]. The slowness of chemisorption is due to the presence of adsorbed oxygen in the investigated range of φ_r [8]. An increase in temperature leads to accelerated chemisorption and a change in the limiting stage of the process at low φ_r. As far as we can judge from the slope of the (log i, φ) curve the process may be determined, for example, by the reaction of the chemisorption products of methanol with OH_{ad} (or O_{ads}). At higher φ_r, the velocity-determining stage is again chemisorption of methanol, and the velocity is les on Ru than on Pt.

According to Petrii [5], maximum catalytic activity at 20°C is exhibited by a Pt + Ru electrode containing 10-15% ruthenium. On alloys with higher Ru contents (25%) the process is more rapid at low φ_r, but slower at high φ_r owing to slower chemisorption of methanol on an electrode with a high Ru content (Fig. 2). The increase in the chemisorption rate with rising temperature has the effect that at 75°C at all i values the overvoltage is less on an alloy with 25% ruthenium.

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* We thank V. F. Stenin and B. I. Podlovchenko for advice concerning the analytical procedure.

† φ_r denotes the potential relative to a reversible hydrogen electrode in the same solution at the experimental temperature.

‡ We thank M. R. Tarasevich for determining the surface area of the Pt + Ru catalyst by the BET method.

M. V. Lomonosov Moscow State University. Translated from Élektrokhimiya, Vol. 4, No. 6, pp. 678-681, June, 1968. Original article submitted July 14, 1967.

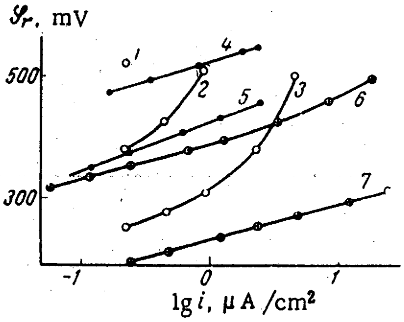

Fig. 1

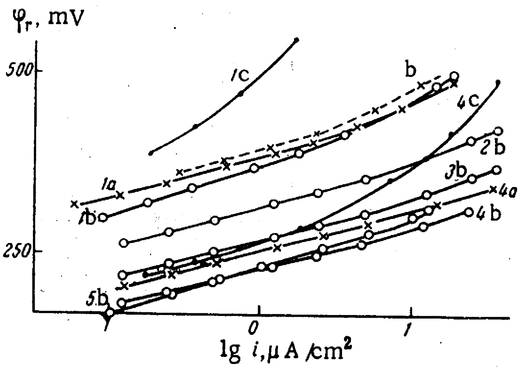

Fig. 2

Fig. 1. Stationary polarization curves of electrooxidation of methanol on an Ru electrode at 22°C (1), 40° (2), and 72° (3); on a Pt/Pt electrode at 22° (4), 80° (5) (from data of Stenin and Podlovchenko [9]); on a 10% Pt + Ru electrode at 22° (6), and on a 25%Pt + Ru electrode at 73° (7). Electrolyte 2 N H_2SO_4 + 2 M CH_3OH.

Fig. 2. Stationary polarization curves of electrooxidation of methanol on Pt + Ru alloys with 10% Ru (a), 25% Ru (b), and 40% Ru (c) at 22°C (1a, 1b, 1c), 42° (2b), 58° (3b), 73 and 75°C (4a, 4b, 4c). Curve 5 was recorded on an electrode kept for a month in a methanol solution at φ_r = 200-300 mV. Curve 5b was recorded at 75°C on a Pt + Ru alloy (25% Ru), deposited on titanium carbide. Electrolyte 2 N H_2SO_4 + 2 M CH_3OH.

With $i < 0.5\ \mu A/cm^2$ on 10 and 25% emd we observe a linear relationship between log i and φ_r, the slopes of the straight lines decreasing from 60-62 to 53-55 mV with increasing temperature. Because of this change in slope, calculation of E_a from the formula $E_a = R[\partial \ln i/\partial(1\ T)]\ \varphi_r$ is approximate and the (E_a, φ_r) curve is anomalous. We thus obtained the following E_a values: 19.5 kcal/mole at 250 mV and 20.3 kcal/mole at 350 mV for 10% emd and 19.6 kcal/mole at 300 mV and 22.8 kcal/mole at 400 mV for 25% emd. On Pt/Pt [9] E_a is 21.8 to 23.4 kcal/mole at 350 mV and 15-15.5 kcal/mole at 500 mV. The cause of the decrease in slope of the (log i, φ_r) curve on the Pt + Ru of emd is not clear. It may be due to the fact that at higher temperatures the process now takes place at the φ_r of the hydrogen sector. On the other hand, oxidation of methanol may take place by several parallel ways [2, 10]. If we assume that one of the reactions is characterized by a stronger dependence on φ_r and the part played by this process in the over-all reaction velocity increases with the temperature, we can explain the decrease in the slope. Note that in the electrooxidation of methanol in acid solutions we do in fact observe (log i, φ_r) curves with slopes of ~60 mV (Pt) [11] and ~30 mV (Rh) [12].

The possibility that electrooxidation of methanol on Pt + Ru electrodes takes place by different routes on different sectors of the surface ensues from analysis of the liquid phase (Table 1 compares these results with data for a Pt/Pt electrode [2]).

Formation of HCHO and HCOOH in the initial moment of electrolysis can be explained if we assume that oxidation of the firmly chemisorbed particles of composition HCO, which largely cover the surface [13], is accompanied by parallel oxidation of the weakly adsorbed particles with different compositions and different strengths of the bond with the surface. Removal of these particles during washing is the cause of the higher oxidation overvoltage of the chemisorbed substance in comparison with that observed in the presence of methanol in the solution [14]. The role of the strongly chemisorbed particles therefore reduces mainly to the fact that they block part of the surface. The results of the analysis in acid agree with those in alkali, thus confirming Petrii's inference [5] that the laws of methanol oxidation on Pt + Ru are simpler than those for Pt/Pt. This probably due to the similar surface states of a Pt + Ru electrode in acid and alkali solutions, due to marked overlapping of the hydrogen and oxygen adsorption sectors in both cases [8].

With aging of Pt + Ru emd in the course of the work, the catalyst activity per 1 cm^2 of true surface decreases somewhat; this can be seen from Fig. 2 which plots the (log i, φ_r) curve on emd, kept at 20°C for a month in a methanol solution with φ_r ~ 200-300 mV.

We performed several experiments with Pt + Ru electrodes, deposited by the method in [5] on a titanium carbide plate. The charging curves on such electrodes differ little from those of Pt + Ru electrodes with a Pt base.

TABLE 1

Solution	Electrode	φ_r, mV	Current yield, %		
			HCHO	HCOOH	CO_2 (by difference)
1 *N* H_2SO_4 + 0,5 *M* CH_3OH	Pt	520—530	2,5—3,0	9—11	86—88
	Pt + Ru (10%)	360—370	2,5	11	86,5
1 *N* KOH + 0,5 *M* CH_3OH	Pt	453—465	1,0	68—71	31—28
	Pt + Ru (10%)	325—335	1,0	14±3	82—85

However, in the case of deposition on titanium carbide we were able to obtain electrodes with somewhat more developed surfaces (roughness factor ~2500 as against ~1500-2000). When we calculated the value of i per true surface area, the (log i, φ_r) curves of methanol oxidation on these electrodes virtually coincided with those on Pt + Ru electrodes deposited on platinum (Fig. 2).

We thank Academician A. N. Frumkin for discussing the experimental results.

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