

DETERMINATION OF THE COMPOSITION OF THE PRODUCTS CHEMOSORBED ON THE SURFACE OF PLATINIZED PLATINUM IN SOLUTIONS OF METHANOL, BY THE METHOD OF CHARGING CURVES

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It is known [1, 2] that a layer of firmly adsorbed substances is formed on the surface of a Pt/Pt-electrode in solutions of organic compounds. It is assumed in most works [1-5] that molecules of the initial substance, which have not undergone and significant changes during the process of adsorption, are present on the electrode (it is believed that the molecular dimensions, its dipole moment, etc. remain constant). However, certain authors [6, 7] have noted that chemisorption on the surface of Pt/Pt of the products of profound decomposition of the initial molecules can also be expected, and the recently appeared work [8] cites a number of experimental results in favor of this hypothesis. The latter viewpoint all the more requires further experimental verification since the adsorption of decomposition products of hydrocarbons and alcohols on surfaces of various catalysts when these hydrocarbons and alcohols are present in the gaseous phase can be considered a well-established fact [9-13]. The purpose of this work was to elucidate the nature of the particles firmly chemisorbed on Pt/Pt in methanol solutions.

The experimental procedure and characteristics of the electrode were described in [14]. The background electrolyte in all the experiments cited was 0.1 N H_2SO_4 . The methanol used (grade "chemically pure") was supplementarily distilled on a rectification column or distilled on a dephlegmator. Both methanol samples gave the same results. The values of the potential φ_r are given with respect to a reversible hydrogen electrode in the same solution. The electrode potentials at which the methanol was introduced are denoted as φ_r^0 , while the values of φ_r established in its presence are denoted as φ'_r . The electrode potential was considered established when changes it it did not exceed 0.1-0.2 mV/min., for which 40-60 min were usually required in rather concentrated methanol solutions (0.1-3M).

When methanol is introduced into the solution bathing a Pt/Pt-electrode, polarized to potentials of the "double layer region," a displacement of the potential in the negative direction to 85 (± 10) mV is observed (Table 1). In contrast to C_4H_9OH , C_3H_7OH and C_2H_5OH [15], methanol, when introduced at φ_r^0 close to zero gives no displacement of φ_r in the positive direction. Thus, it can be considered that when $\varphi_r > 0$, only the process of oxidation of CH_3OH takes place at an appreciable rate on Pt/Pt at room temperature. It is further assumed that the displacement of φ_r in the negative direction and the appearance of adsorbed hydrogen on the surface of Pt after the introduction of CH_3OH are related to dehydrogenation of the alcohol molecules.* However, the mechanism of the appearance of H_{ads} for the problem under consideration is of no theoretical significance.

The charging curve after washing of methanol from the electrode (curve 1 of Fig. 1) contains two lags, one of which (a) corresponds to the oxidation of adsorbed hydrogen, the other (b) to the oxidation of a firmly chemisorbed substance (the physically adsorbed and insufficiently firmly chemisorbed molecules of CH_3OH are apparently removed during the washing process). We can consider that all the chemisorbed substance is oxidized up to 700 mV (at $i = 1 \cdot 10^{-4}$ A/cm² of visible surface), so that the charging curve of Pt (CH_3OH)_{ads} and the charging curve in 0.1 N H_2SO_4 (curves 1 and 1a of Fig. 1) coincide at higher potentials. Table 1 presents the values of the ratios of the hydrogen lag† and the lag corresponding to the oxidation of chemisorbed CH_3OH on the charging curve of Pt- $(CH_3OH)_{ads}$ (the CH_3OH concentration after the introduction comprised 0.7 M) to the hydrogen lag on the charging curve in pure 0.1 H_2SO_4 (these quantities will be denoted as m and k, respectively) as a function of φ_r^0 . As can be

*Evidence in favor of this hypothesis will be cited in another work.

†In calculating the hydrogen lags, the initial portions and linear portions of the "double layer region" of the corresponding charging curves were extrapolated to $\varphi_r = 0$.

TABLE 1

φ_r^0 , mV	φ_r^1 , mV	-k	m	φ_r^0 , mV	φ_r^1 , mV	k	m
995	106	0.61	0.39	425	80	0.50	0.57
745	88	0.47	0.565	312	83	0.38	0.64
571	80	0.47	0.55	151	67	0.18	0.76
500	81	0.44	0.59	53	47	0.02	0.96
490	86	0.44	0.54	0	0	0	1

TABLE 2

Exp. No.	CH ₃ OH, mole/liter	φ_r^0 , mV	Δt , min	φ_r min, mV	k	m'	k/m'	Q_H^0 , C/cm ²	$\Delta\varphi_r$ wash, mV
1	3	509	46	53	0,43	0,454	0,95	0,242	+29
2	0,5	511	70	80	0,44	0,44	1,0	0,192	+8
3	0,5	490	37	86	0,44	0,39	1,13	0,181	+9
4	0,1	515	78	97	0,398	0,414	0,96	0,204	+4
5	0,01	510	113	128	0,360	0,324	1,11	0,204	+3
6	0,1	508	2	160	0,285	0,293	0,97	0,204	+6
7	0,001	509	221	171	0,294	0,260	1,13	0,214	+2
8	0,001	508	100	194	0,259	0,21	1,23	0,214	+2
9	0,01	510	3	231	0,177	0,165	1,07	0,204	+6
10	0,001	706	8	297	0,139	0,088	1,58	0,204	+1

seen from the data of Table 1, the amount of the chemisorbed product is practically independent of φ_r^0 in the region of 350-750 mV, gradually drops at φ_r^0 below 350 mV, and is equal to zero at $\varphi_r^0 = 0$. If hydrogen is passed through the solution after the introduction of methanol at φ_r of the "double electric layer" or the electrode is cathode-polarized by a small current (for example, $1 \cdot 10^{-4}$ A/cm²), the electrode acquires a zero potential. However, the amount of the chemisorbed product is reduced by almost 10-20% as a result of these operations ($k = 0.38-0.41$).

The observed dependence of the amount of the chemisorbed substance on φ_r^0 and on the order of introduction of the electrolyte in contact with methanol and hydrogen apparently should be explained by the fact that the rate of the chemisorption process drops rather rapidly with decreasing φ_r of the Pt/Pt electrode. Since according to [14], the latter condition is satisfied by the process of dehydrogenation of the alcohol molecules, the experimental material cited above is in good agreement with the hypothesis that dehydrogenation products of methanol are chemisorbed on the Pt/Pt surface. Then at φ_r^0 of the hydrogen lag* obviously a smaller value of k should correspond to the lower value of the displacement of φ_r after the introduction of CH₃OH, which is also observed experimentally (Table 1). At $\varphi_r^0 = 0$, methanol is not dehydrogenated at an appreciable rate, and $k = 0$. At φ_r^0 corresponding to the oxygen region of the charging curve, part of the chemisorbed product is formed as a result of oxidation of CH₃OH by the adsorbed oxygen, which also explains the large value of the quantity k at $\varphi_r^0 = 995$ mV.

The products of the dehydrogenation of methanol chemisorbed on the Pt/Pt surface in methanol solutions practically do not enter into the reverse reaction with hydrogen. Carbon monoxide, which is chemisorbed on a nickel catalyst in the presence of alcohols in the gaseous phase [13] behaves analogously. The dehydrogenation products of hydrocarbons, chemisorbed on the surfaces of Ni and Rh catalysts existing in contact with the gaseous phase, are capable of reacting with hydrogen, and thus can be removed from the surface of the catalyst [10, 11]. It is possible that a stronger chemisorption is characteristic of particles containing oxygen.

A number of conclusions on the nature of the particles chemisorbed on the Pt/Pt surface in the presence of CH₃OH were permitted by adsorption measurements in dilute methanol solutions. At concentrations of $1 \cdot 10^{-3}$ - $1 \cdot 10^{-1}$ M CH₃OH, the change in φ_r with time becomes comparatively small for φ_r still differing substantially from φ_r^1 . This made it possible to wash the electrode at various φ_r after the introduction of CH₃OH, so that the displacements of φ_r during the washing process were negligible. The results of such experiments are collected in Table 2.

* At φ_r^0 of the "double layer region" this effect is difficult to detect on account of the low capacitance of the electrode.

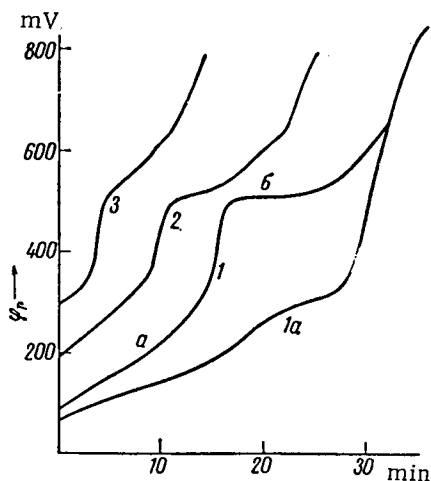


Fig. 1. Charging curves in 0.1 N H_2SO_4 after washing of Pt/Pt-electrode to remove the solutions: 1) 0.1 N H_2SO_4 + 0.5 M CH_3OH ; 2, 3) 0.1 N H_2SO_4 + 0.001 M CH_3OH . Potentials of the beginning of washing: 1) 82 mV; 2) 196 mV; 3) 298 mV; 1a—direct path of the charging curve in pure 0.1 N H_2SO_4 . $i = 1 \cdot 10^{-4}$ A/cm² of visible surface.

The following new notations were introduced in Table 2: Δt —the time from the moment of introduction of the substance until the beginning of washing, $\varphi_{\text{r min}}$ —minimum value* of φ_{r} observed experimentally. The coefficient m' is equal to the ratio of the quantity H_{ads} , determined according to the corresponding charging curve of $\text{Pt}(\text{CH}_3\text{OH})_{\text{ads}}$ (for example, curves 1, 2, 3 of Fig. 1) by extrapolating the hydrogen lag and linear portion of the double layer region to $\varphi_{\text{r min}}$, to the amount of adsorbed hydrogen at $\varphi_{\text{r}} = 0$ in pure 0.1 N H_2SO_4 , Q_{H}^0 (all the values of the adsorption are expressed in electrical units). $\Delta\varphi_{\text{r wash}}$ represents the magnitude of the displacement of φ_{r} with respect to $\varphi_{\text{r wash}}$ in the washing process. The small values of $\Delta\varphi_{\text{r wash}}$ in all the experiments except for experiment 1 give evidence that the entry of oxygen into the system during the washing process was almost entirely excluded. The substantial $\Delta\varphi_{\text{r wash}}$ in 3M CH_3OH is evidently related to the low value of φ_{r}^0 in the solution. As can be seen from Table 2, independent of the CH_3OH concentration and the potentials at which the washing was performed, the amount of the adsorbed organic substance and hydrogen are always approximately

proportional with a coefficient of proportionality, ~ 1 ($k \approx m'$). The values of the coefficients k and m' are actually determined only by the values of $\varphi_{\text{r min}}$ and, all the more, the lower the $\varphi_{\text{r min}}$ observed experimentally (the experiments in Table 2 are arranged in order of increasing $\varphi_{\text{r min}}$).

To explain the experimental results obtained, we should assume that the processes of fitting of hydrogen and the chemisorbed substance are related by one act; apparently decomposition of the CH_3OH molecule into the chemisorbed particle and H_{ads} . Then, if any one dehydrogenation product of CH_3OH is chemisorbed on the surface of Pt/Pt, and its oxidation proceeds to CO_2 during the taking of the charging curve, we should expect that the ratio of the amount of the adsorbed substance to the amount of hydrogen liberated as a result of dehydrogenation of methanol will be expressed by a ratio of simple whole numbers n_1 and n_2 ($n_1 + n_2 = 6$).

The ratio indicated above will be somewhat smaller than the quantity k/m' , since a certain correction $\Delta m'$ for H_{ads} that went for discharging of the electric double layer should be introduced into the value of m' . It is rather difficult to calculate H_{ads} accurately, since the values of the double layer capacitance of the electrode during the process of displacement of φ_{r} are unknown. Approximate calculation shows that when $m' \geq 0.3$, this correction apparently should not exceed 20% of the value of m' , a consideration of this correction leads to values of $k/m' + \Delta m'$ closer to 1 than the values of k/m' cited in Table 2 (especially for experiment 10). Consequently, considering the fact that the oxidation of the substance chemisorbed in the presence of the substance chemisorbed in the presence of CH_3OH proceeds to CO_2 ,† we can assume that under the conditions considered, the CH_3OH molecules primarily give off three hydrogen atoms upon decomposition, and a particle of the type $\text{O}-\text{C}-\text{H}$ is chemisorbed on the Pt/Pt

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surface (in our opinion, the absorption of particles $(\text{COH})_{\chi}$, where $\chi > 1$, is relatively improbable). A more accurate explanation of the composition and structure of the chemisorbed particles requires a further experimental investigation. According to the data of Table 1, the sum of the coefficients k and m at various φ_{r}^0 is close to one. This permits us to assume that the chemisorbed particle will occupy just as many hydrogen places (Pt atoms) as it gives off electrons upon oxidation. Considering that $n = 3$, we obtain the fact that the chemisorbed particle occupies approximately $23 \text{ \AA}^2$.

* When the washing was begun at φ_{r} higher than φ_{r}^0 , during the first washings in spite of the fact that they were performed as fast as possible, the electrode potential was still somewhat displaced in the cathode direction. However, the difference between $\varphi_{\text{r min}}$ and φ_{r} of the beginning of washing did not exceed 10 mV in all the experiments cited.

† As the investigation showed, the oxidation of the substances chemisorbed on Pt/Pt in the presence of H_2CO and HCOOH occurs in the same potential region as the oxidation of the chemisorbed dehydrogenation product of CH_3OH .

Pavela [2] (Pt/Pt) and Breiter [16] (smooth Pt) believed that physically adsorbed methanol is present on the surface of the electrode in CH_3OH solutions, and found the "equilibrium" isotherms of its adsorption. According to the above, the data on the adsorption of CH_3OH obtained by Pavela under conditions close to ours apparently pertain to the chemisorbed products of its decomposition, and should be explained by the kinetics of the dehydrogenation of CH_3OH . In spite of the specifics of the anode pulse method used in [16], at the present time it likewise cannot be stated with complete assurance that their adsorption measurements pertain to adsorbed CH_3OH and do not include to a significant degree the chemisorbed products of its oxidation, as the authors propose. * Let us express our profound gratitude to academician A. N. Frumkin for his constant attention and consultation in this work.

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