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Abstract

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

(Presented by Academician A. N. Frumkin, February 10, 1964)

It is known (^{1,2}) that on the surface of a Pt/Pt electrode in solutions of organic compounds layers of strongly adsorbed substances are formed. In most works ($^{1-5}$) it is assumed that molecules of the initial substance are present on the electrode, having undergone no significant changes in the adsorption process (it is considered that the dimensions of the molecule, its dipole moment, etc., remain constant). However, some authors (^{6,7}) have noted that chemisorption on the Pt/Pt surface and the products of deep decomposition of the initial molecules may be expected, and in a recently published work (^{8}) a number of experimental results are given in favor of this assumption. The latter point of view all the more requires further experimental verification, since adsorption on the surfaces of various catalysts of the decomposition products of hydrocarbons and alcohols in the presence of the latter in the gas phase may be regarded as a well-established fact ($^{9-13}$). The purpose of the present work was to clarify the nature of the particles strongly chemisorbed on Pt/Pt in methanol solutions.

The experimental procedure and the characteristics of the electrode are described in (^{14}). The background electrolyte in all the experiments presented was 0.1 N H_2SO_4. The methanol used (reagent grade) was additionally purified on a rectification column or distilled on a dephlegmator. Both methanol samples gave identical results. The values of the potential φ_r are given relative to the reversible hydrogen electrode in the same solution.

Table 1

φ_r^0, mV	φ_r', mV	k	m	φ_r^0, mV	φ_r', 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

φ_r^0, mV	φ'_r, mV	k	m	φ_r^0, mV	φ'_r, mV	k	m
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

The electrode potentials at which methanol was introduced are denoted by φ_r^0, and the values of φ_r established in its presence by φ'_r. The electrode potential was considered established when its change did not exceed 0.1–0.2 mV/min; for this purpose, in sufficiently concentrated methanol solutions (0.1–3 M), usually 40–60 min were required.

Upon introducing methanol into the solution washing a Pt/Pt electrode polarized to potentials of the "double-layer region," a shift of the potential in the negative direction by up to 85(±10) mV is observed (Table 1). Unlike C_4H_9OH, C_3H_7OH, and C_2H_5OH (^{15}), methanol, when introduced at φ_r^0 values close to 0, does not give a shift of φ_r in the positive direction. Thus, it may be considered that at $\varphi_r > 0$ on Pt/Pt at room temperature only the oxidation process of CH_3OH proceeds at an appreciable rate. In what follows it is assumed that the displacement of φ_r in the negative direction and the appearance of adsorbed hydrogen on the Pt surface after the introduction of CH_3OH are connected with dehydrogenation of the alcohol molecules.* However, the mechanism of appearance of H_{ads} is not of fundamental importance for the problem under consideration.

* Arguments in favor of this assumption will be presented in another paper.

On the charging curve after washing the electrode free of methanol (curve 1 in Fig. 1) there are two arrests, one of which (a) corresponds to the oxidation of adsorbed hydrogen, and the other (b) to the oxidation of a strongly chemisorbed substance (physically adsorbed and insufficiently strongly chemisorbed CH_3OH molecules are apparently removed during washing). It may be assumed that all the chemisorbed substance is oxidized up to 700 mV (at $i = 1 \cdot 10^{-4}$ A/cm^2 of apparent surface), since the charging curve of $Pt(CH_3OH)_{ads}$ and the charging curve in 0.1 N H_2SO_4 (curves 1 and 1a in Fig. 1) coincide at higher potentials. Table 1 gives the values of the ratios of the magnitudes of the hydrogen arrest and of the arrest corresponding to the oxidation of chemisorbed CH_3OH on the charging curve of $Pt(CH_3OH)_{ads}$ (the CH_3OH concentration after introduction was 0.7 M) to the magnitude of the hydrogen arrest on the charging curve in pure 0.1 N H_2SO_4* (we shall denote these quantities, respectively, by m and k), as a function of φ_r^0. As is seen from the data of Table 1, the amount of chemisorbed product is practically independent of φ_r^0 in the range 350-750 mV, decreases gradually when φ_r^0 is below 350 mV, and at $\varphi_r^0 = 0$ is equal to zero. If, after introducing methanol at φ_r of the "double electric layer," hydrogen is passed through the solution or the electrode is polarized cathodically with a small current (for example, $1 \cdot 10^{-4}$ A/cm^2), the electrode acquires a zero potential. However, the amount of chemisorbed product as a result of these operations decreases by only 10-20% ($k = 0.38$-0.41).

The observed dependence of the amount of chemisorbed substance on φ_r^0 and on the sequence in which the electrode is brought into contact with methanol and hydrogen should apparently be explained by the fact that the rate of the chemisorption process decreases rather rapidly with decreasing φ_r of the Pt/Pt electrode. Since, according to work ([14]), the process of dehydrogenation of alcohol molecules satisfies the latter condition, the experimental material presented above is in good agreement with the supposition that products of methanol dehydrogenation are chemisorbed on the Pt/Pt surface. Then, at φ_r^0 of the hydrogen arrest,** a smaller shift of φ_r after introduction of CH_3OH should obviously correspond to a smaller value of k, as is observed experimentally (Table 1). At $\varphi_r^0 = 0$, methanol is not dehydrogenated at an appreciable rate and $k = 0$. At φ_r^0 values corresponding to the oxygen region of the charging curve, part of the chemisorbed product is formed as a result of oxidation of CH_3OH by adsorbed oxygen, which explains the larger value of k at $\varphi_r^0 = 995$ mV.

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

A number of conclusions about the nature of the particles chemisorbed on the Pt/Pt surface in the presence of CH_3OH made it possible to carry out adsorption measurements in dilute methanol solutions. At concentrations of $1 \cdot 10^{-3}$-$1 \cdot 10^{-1}$ M CH_3OH, the change of φ_r with time becomes comparatively small at φ_r still considerably different from φ_r'. This made it possible–

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

** At φ_r^0 of the "double-layer region," this effect is difficult to detect because of the small capacitance of the electrode.

it possible to rinse the electrode at various φ_r after the introduction of CH_3OH in such a way that the shifts of φ_r during the rinsing process were insignificant. The results of such experiments are collected in Table 2.

Table 2

Experiment no.	Conc. CH_3OH, mol/l	φ_r^0, mV	Δt, min	$\varphi_{r\,\mathrm{min}}$, mV	k	m'	k/m'	Q_H^0, coul/cm^2	$\Delta\varphi_{r\,\mathrm{rinse}}$, 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

The following new designations are introduced in Table 2: Δt is the time from the moment of introduction of the substance to the beginning of rinsing; $\varphi_{r\,\mathrm{min}}$ is the minimum value* of φ_r observed in the experiment. The coefficient m' is equal to the ratio of the amount of H_{ads}, determined from the corresponding charging curve of $Pt(CH_3OH)_{ads}$ (for example, curves 1, 2, 3 in Fig. 1) by extrapolation of the hydrogen-delay and the linear segment of the double-layer region to $\varphi_{r\,\mathrm{min}}$, to the amount of adsorbed hydrogen at $\varphi_r = 0$ in pure 0.1 N H_2SO_4, Q_H^0 (all adsorption quantities are expressed in electrical units). $\Delta\varphi_{r\,\mathrm{rinse}}$ is the magnitude of the shift of φ_r relative to $\varphi_{r\,\mathrm{rinse}}$ during rinsing. The small values of $\Delta\varphi_{r\,\mathrm{rinse}}$ in all experiments except experiment 1 indicate that the entry of oxygen into the system during rinsing was practically completely excluded. The considerable $\Delta\varphi_{r\,\mathrm{rinse}}$ in 3M CH_3OH is evidently associated with the low value of φ_r' in this solution. As is seen from Table 2, independently of the concentration of CH_3OH and of the potentials at which rinsing was carried out, the amounts of adsorbed organic substance and hydrogen are always approximately proportional, with a proportionality coefficient ~ 1 ($k \simeq m'$). The values of the coefficients k and m' are in fact determined only by the values of $\varphi_{r\,\mathrm{min}}$, and the larger they are, the lower the $\varphi_{r\,\mathrm{min}}$ observed in the experiment (the experiments in Table 2 are arranged in order of increasing $\varphi_{r\,\mathrm{min}}$).

Fig. 1. Charging curves in 0.1 N H_2SO_4 after rinsing a Pt/Pt electrode from 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 at the beginning of rinsing: 1 –82 mV; 2 –196 mV; 3 –298 mV; 1a –direct course of the charging curve in pure 0.1 N H_2SO_4. $i = 1 \cdot 10^{-4}$ A/cm^2 of visible surface.

To explain the experimental results obtained, it should be assumed that the processes of deposition of hydrogen and of the chemisorbed substance are connected with one another by a single act: apparently, by the decomposition of the CH_3OH molecule into a chemisorbing particle and H_{ads}. Then, if on the surface

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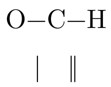
Figure 1: Fig. 1. Charging curves in 0.1 N H2SO4 after rinsing a Pt/Pt electrode from solutions: 1 –0.1 N H2SO4 + 0.5 M CH3OH; 2, 3 –0.1 N H2SO4 + 0.001 M CH3OH. Potentials at the beginning of rinsing: 1 –82 mV; 2 –196 mV; 3 –298 mV; 1a –direct course of the charging curve in pure 0.1 N H2SO4. i = 1 · 10^-4 A/cm^2 of visible surface

on Pt/Pt some single product of the dehydrogenation of CH_3OH is chemisorbed, and its oxidation when the charging curve is recorded proceeds to CO_2, one should expect that the ratio of the amount of adsorbed substance to the amount of hydrogen evolved as a result of methanol dehydrogenation will be expressed by the ratio of simple integers n_1 and n_2 $(n_1 + n_2 = 6)$.

The ratio indicated above will be somewhat smaller than the value k/m', since a certain correction $\Delta m'$ must be introduced into the value m' for H_{ads} consumed in discharging the electrical double layer. It is rather difficult to calculate the latter quantity sufficiently accurately, since the values of the double-layer capacitance of the electrode during the displacement process φ_r are unknown. An approximate calculation shows that this correction at $m' \geq 0.3$, apparently, should not exceed 20% of the value of m'; at smaller values of m', taking this correction into account gives values of $k/m' + \Delta m'$ closer to 1 than the values of k/m' given in Table 2 (especially for experiment 10). Consequently, assuming that oxidation of the substance chemisorbed in the presence of CH_3OH proceeds to CO_2*, one may suppose that, under the conditions considered, CH_3OH molecules, upon decomposition, predominantly give up 3 hydrogen atoms, and on the Pt/Pt surface a particle of the type



$$\begin{array}{c} O-C-H \\ |\quad\| \end{array}$$

is chemisorbed (in our view, adsorption of particles $(COH)_x$, where $x > 1$, is unlikely). A more exact elucidation of the composition and structure of the chemisorbing particles requires further experimental study. According to the data of Table 1, the sum of the coefficients k and m at different φ_r^0 is close to

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* When rinsing began at a φ_r higher than φ_r', during the first rinses, despite the fact that they were carried out as rapidly as possible, the electrode potential nevertheless shifted somewhat to the cathodic side. However, the differences between $\varphi_{r\,\min}$ and φ_r at the beginning of rinsing in all the experiments cited did not exceed 10 mV.

1. This allows one to assume that the chemisorbed particle occupies as many hydrogen sites (Pt atoms) as electrons it gives up during oxidation. Taking $n = 3$, we obtain that the chemisorbed particle occupies approximately 23 $\mathring{A}^2$.

Pavela (2) (Pt/Pt) and Breiter (16) (smooth Pt) believed that physically adsorbed methanol is present on the electrode surface in CH_3OH solutions, and found "equilibrium" isotherms of its adsorption. According to the above considerations, the data on CH_3OH adsorption obtained by Pavela under conditions close to ours in fact apparently refer to the chemisorbed products of its decomposition and should be explained by the kinetics of CH_3OH dehydrogenation. Despite the specific nature of the anodic-pulse method used in (16), at present one likewise cannot say with complete certainty that their adsorption measurements relate only to adsorbed CH_3OH and do not include, to a significant extent, chemisorbed products of its oxidation, as the authors suppose**.

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* As the study showed, the oxidation of 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.

** An analogous remark concerning the data of Breiter and Gilman was expressed in work ([8]).

Note: Figure translations are in progress. See original paper for figures.

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