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Abstract

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THE INFLUENCE OF pH ON THE ADSORPTION OF HYDROGEN BY PLATINIZED PLATINUM

The question of the influence of the pH of the medium on the adsorption of hydrogen by catalysts is of substantial interest for elucidating the kinetics and mechanism of liquid-phase hydrogenation. By the charging-curve method ([1]-[2]) it has been established that the binding energy of hydrogen adsorbed by platinized platinum depends on the nature of the electrolyte and on the composition of the electric double layer at the metal–solution interface. Thus, in 0.1 N H_2SO_4 the hydrogen region on the charging curve ends at a potential of +0.35 V*, whereas in 1 N KOH it ends at +0.41 V. Thus, in an alkaline medium the binding energy of hydrogen with the platinum surface is higher than in an acidic one. In the hydrogenation of a number of unsaturated compounds it has been established ([3]-[12]) that the pH of the medium affects the rate and direction of the process.

However, the influence of the pH of the medium on the amount of adsorbed hydrogen and on its binding energy with the catalyst surface has not been sufficiently studied.

Recording charging curves for rhodium black in an H_2SO_4 + Na_2SO_4 solution at a constant concentration of SO_4^{2-} (pH 0.1–4.1), and also in alkali solutions, showed ([13]) that with increasing pH the binding energy of hydrogen with the electrode surface and the adsorption capacity per unit surface area of rhodium increase. Analogous phenomena are also observed when recording charging curves for ruthenium ([14]).

In the present work the influence of the pH of the medium on the adsorption of hydrogen by platinized platinum has been studied by the charging-curve method ([1], [2]). Two series of experiments were carried out. In the first series of experiments the electrolytes were solutions of H_2SO_4, KOH, and K_2SO_4 with different pH values, at a constant and equal 0.1 N concentration of SO_4^{2-} ions. As the electrode, a Pt gauze with a visible surface area of 16 cm^2 was used. The true surface area of the electrode after platinization, calculated from the double-layer capacity in 0.1 N H_2SO_4 (the capacity of 1 cm^2 was taken as 36 μF), was 11,000 cm^2. Polarization was carried out at a current density of $6 \cdot 10^{-5}$ A/cm^2 of the visible surface of the electrode; the temperature of the experiments was 19–

20°. The results of this series of experiments are presented in Fig. 1 and Table 1. As is seen from Fig. 1, the extent of the hydrogen region on the charging curves in sulfate solutions increases with increasing pH, which indicates an increase in the amount of hydrogen sorbed by platinum.

The desorption potential of hydrogen (E of H_2 desorption, V), and consequently also the binding energy of hydrogen with the electrode, as is seen from the data of Table 1, increases; at the same time the amount of electricity expended in removing adsorbed hydrogen from the electrode (Q of H_2 desorption, C) also increases, which indicates an increase in the degree of filling of the platinum surface with hydrogen. The degree of filling of the electrode surface with hydrogen ($\theta, \%$) was calculated from the "true surface" of the electrode, determined from the double-layer capacity in 0.1 N H_2SO_4.

* All potential values are given relative to the reversible hydrogen electrode in the same solution.

As shown in work (15), calculation of the true surface area of the electrode from the double-layer capacitance in sulfuric-acid solutions is quite reliable and gives results that practically coincide with the results of determining the surface area by the BET method.

The second series of experiments was carried out with the same electrode, but a Britton–Robinson buffer solution (16) was used as the electrolyte, consisting of a mixture of 0.04 M H_3BO_3, 0.04 M H_3PO_4, and 0.04 M CH_3COOH; the pH was varied by adding 4 N KOH to the buffer solution.

Table 1

Electrochemical characteristics of the electrode in sulfate solution

pH	E of H_2 desorption, V	Q of H_2 desorption, C	Number of H atoms removed from the surface $n \cdot 10^{-18}$	Surface coverage by hydrogen θ, %
1	0.33	0.93	5.9	45.5
3	0.35	0.99	6.2	47.5
5	0.37	1.05	6.6	50.5
7	0.38	1.10	6.9	52.5
10	0.40	1.15	7.2	55.0
13	0.42	1.22	7.7	59.0

The anions of such a solution were not specifically adsorbed on the electrode surface (7). The experiments were carried out in the pH range 2.0–13.0. The results of the experiments are presented in Fig. 2. From the data obtained it is

Fig. 1. Charging curves of platinized platinum in sulfuric-acid solution at different pH: 1 –1.0; 2 –3.0; 3 –5.0; 4 –7.0; 5 –10.0; 6 –13.0

Figure 1: Fig. 1. Charging curves of platinized platinum in sulfuric-acid solution at different pH: 1 –1.0; 2 –3.0; 3 –5.0; 4 –7.0; 5 –10.0; 6 –13.0

Fig. 2. Charging curves of platinized platinum in buffer solution at different pH: 1 –2.0; 2 –4.5; 3 –6.5; 4 –8.5; 5 –11.0; 6 –13.0

Figure 2: Fig. 2. Charging curves of platinized platinum in buffer solution at different pH: 1 –2.0; 2 –4.5; 3 –6.5; 4 –8.5; 5 –11.0; 6 –13.0

evident that, when one electrolyte is replaced by another, the general regularities associated with the influence of pH on hydrogen adsorption on platinum remain the same. As in sulfate solutions, with increasing pH the potential at which the hydrogen region on the curves ends increases, which indicates an increase in the strength of the electrode-hydrogen bond.

It should be noted that, in order to obtain reproducible curves in buffer solutions, it is necessary during polarization to stir the electrolyte vigorously by passing a stream of inert gas (argon) through it. Without stirring the electrolyte with argon, the charging curves are shortened along the abscissa axis, the potential values are unstable; after the anodic polarization is switched off, the electrode potential slowly returns to its initial value, and between the curves for the forward and reverse course of polarization there is a considerable gap, reaching 0.3 V.

Fig. 1. Charging curves of platinized platinum in sulfuric-acid solution at different pH: 1 –1.0; 2 –3.0; 3 –5.0; 4 –7.0; 5 –10.0; 6 –13.0

Fig. 2. Charging curves of platinized platinum in buffer solution at different pH: 1 –2.0; 2 –4.5; 3 –6.5; 4 –8.5; 5 –11.0; 6 –13.0

Stirring the electrolyte with an inert gas considerably increases the stability of the potentials and improves the reversibility of the adsorption curves, reducing the width of the hysteresis "loop" to 0.04–0.05 V.

However, in this case it is evidently impossible to judge the amount of hydrogen adsorbed by the electrode, since the length of the curves along the abscissa axis depends on the rate of stirring of the solution.

The increase in the bond energy of adsorbed hydrogen with increasing pH can be explained by the fact that, as the concentration of hydrogen ions in the solution decreases, the outer plate of the double layer begins to be built up from cations. The presence of cations promotes strengthening of the bond between adsorbed hydrogen and the platinum surface. For the same reason, with increasing pH the capacitance of the electrode in the double-layer region increases [17].

Comparison of the curves in Figs. 1 and 2 shows that the slope of the double-

layer section of the curves in sulfate and buffer solutions is different; this is probably a consequence of the influence of the nature of the electrolyte on the electrical capacitance of platinum in the double-layer region.

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