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Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

Abstract

Full Text

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ON THE CHARGING CURVES OF BORIDE CATALYSTS OF Pt-GROUP METALS

It has recently been established that catalysts prepared by treating aqueous solutions of salts of Pd, Pt, or Rh with sodium or potassium borohydride possess high catalytic activity in reactions of liquid-phase hydrogenation of various organic compounds ([1]). In this connection it was of interest to obtain data characterizing the surface properties of the catalysts. It is known that from charging curves one can judge the magnitude of the catalyst surface and the binding energy of hydrogen with the catalyst. Charging curves can be obtained both by polarization with an electric current and by anodic polarization with organic substances ([2,3]). In the present work both methods were used.

Fig. 1. Charging curves under polarization by electric current in 0.1 N NaOH $(1, 2, 3)$, 0.1 N H_2SO_4 $(4, 6, 8)$, 0.1 N HCl $(5, 7, 9)$: Pt–B $(2, 4, 5)$, Pd–B $(1, 6, 7)$, Rh–B $(3, 8, 9)$

A. The procedure for recording charging curves under anodic polarization by electric current was as follows: after filling the duck-shaped vessel with electrolyte (0.1 N NaOH, 0.1 N HCl, 0.1 N H_2SO_4) and introducing a weighed portion of the catalyst, the shaker was switched on (600 oscillations/min), the system was saturated with hydrogen to the reversible hydrogen potential; the excess hydrogen was displaced by purified nitrogen, and, with a polarizing current of $0.5 \cdot 10^{-3}$ A, charging curves were recorded.

Fig. 2. Charging curves under anodic polarization with phenylacetylene $(2, 4, 6)$ and diphenylacetylene $(1, 3, 5)$: Pt–B $(5, 6)$, Rh–B $(3, 4)$, Pd–B $(1, 2)$

B. The recording of charging curves with organic substances was carried out by the following procedure: the catalyst in solvent (0.1 N HCl in 70% CH_3OH) was saturated with hydrogen to the reversible hydrogen potential; then the hy-

drogen was displaced from the duck-shaped vessel with purified nitrogen, the shaker was started (600 oscillations/min), and a solution of the organic substance (phenylacetylene or diphenylacetylene) was fed into the vessel at a constant rate. The feed rate ensured removal of hydrogen in the equilibrium region (for phenylacetylene $28 \cdot 10^{-5}$ g/min, for diphenylacetylene $34 \cdot 10^{-5}$ g/min).

Figure 1 shows the charging curves of boride catalysts of Pt-group metals (Pd, Pt, Rh). The similarity in the course of the anodic and cathodic curves,

stability of the potential when the current is switched off indicate the reversibility of the process. As can be seen from the figure, in an acidic medium the double-layer region is clearly expressed, whereas in an alkaline medium the curves have a diffuse character, which is associated with the process of oxidation of the catalyst surface. A comparison of the potential intervals of the hydrogen region shows that, with increasing pH, the strength of the binding energy of hydrogen with the catalyst surface increases. On the charging curves no segment of "hydrogen delay" is observed. It should be especially noted that there is no segment of constant potential in the equilibrium region, where a slow, uniform shift of the potential is observed until the transition to the double-layer region. The same pattern in the course of the charging curves was observed for the catalysts Pt/SiO_2 and Pd/SiO_2 ([2]); apparently, the boron introduced into the composition of the catalyst forms a film in the surface layer, affecting the character of the bond of hydrogen with the catalyst surface analogously to the action of the SiO_2 phase.

Table 1

Catalyst	Method	Specific surface area, m^2/g	Amount of sorbed H_2, ml/g
Pd–B	A	48	62
Pd–B	B	42	54
Pd–B	BET	37	–
Pt–B	A	42	35
Pt–B	B	37	32
Pt–B	BET	28	–
Rh–B	A	55	87
Rh–B	B	52	72
Rh–B	BET	44	–

The composition of the electrolyte affects not only the strength of the bond of hydrogen with the catalyst surface, but also the extent of the hydrogen region; apparently, the process of sorption of H_2 is affected by changes in the surface layer that occur when one electrolyte is replaced by another.

If one assumes that the potential at which the curves in different electrolytes begin to diverge is the potential of the end of dissolution, then the curves in

Fig. 3. Isotherms of dissolution of H_2 in Pd–B (1, 2), Pt–B (3, 4), Rh–B (5, 6)

Figure 3: Fig. 3. Isotherms of dissolution of H_2 in Pd–B (1, 2), Pt–B (3, 4), Rh–B (5, 6)

Fig. 1 can be used to compare the character of the sorbed hydrogen. Then, for Pd–B the dissolved hydrogen amounts to 74% of the total amount of sorbed hydrogen, and the adsorbed hydrogen to 26%. For Rh–B, 86% and 14%, and for Pt–B, 32% and 68%, respectively. All the curves presented (Fig. 1) were used to determine the total amount of sorbed hydrogen and the specific surface area (Table 1).

Fig. 3. Isotherms of dissolution of H_2 in Pd–B (1, 2), Pt–B (3, 4), Rh–B (5, 6)

The charging curves recorded by method B (Fig. 2) are in many respects identical with the curves in Fig. 1. As in the preceding case, in the equilibrium region there are no segments with constant potential (a slow uniform shift of the potential to $\Delta E = 0.2$—0.22 V before transition to the double-layer region, $\Delta E = 0.25$—0.50 V). It should be noted that the courses of the charging curves recorded under anodic polarization with phenylacetylene and diphenylacetylene are similar. The charging curves recorded under polarization with phenylacetylene have a character somewhat different from the curve only in the final segment ($\Delta E = 0.45$—0.55 V). This phenomenon is apparently due both to the geometric inaccessibility of the surface hydrogen to the corresponding molecule and to the energetic inhomogeneity of the bound hydrogen. The results of calculations made on the basis of the charging curves (Fig. 2) largely coincide with the results obtained by method A. In Table 1

For comparison, results of measurements of the surface area of boride catalysts by the BET method are given. The satisfactory agreement of the results indicates that the values of the specific surface area are close to the true value.

From the charging curves of the catalysts (Figs. 1 and 2), recorded at 20°, the isotherms of dissolution of H_2 in the boride catalysts were calculated. The equilibrium pressure of the absorbed hydrogen was determined by the Nernst formula. As can be seen from Fig. 3, the isotherms of H_2 dissolved in the boride catalysts, calculated from charging curves recorded both by method A and by method B, are very close to one another.

Thus, the introduction of boron into the composition of Pd, Pt, and Rh catalysts affects the character of the course of the charging curve of the catalysts studied.

The results of the work confirmed the previously expressed assumption concerning the possibility of recording charging curves with compounds of the acetylene type.

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