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Academician of the Academy of Sciences of the Kazakh SSR D. V. Sokolsky and N. F. Noskova

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Abstract

Full Text

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Charging Curves of Skeletal Ni, Pd/$CaCO_3$, and Pt Black under Anodic Polarization by Acetylene

The quantity and quality of gases sorbed by catalysts can be judged from the so-called charging curves. These can be obtained not only by polarization with an electric current, but also with an organic substance. A charging curve under anodic polarization by quinone was recorded [1]. In the present work, charging curves under anodic polarization by acetylene were obtained for skeletal Ni, Pd/$CaCO_3$ (5% Pd), and Pt black, making it possible to determine the amount of adsorbed and occluded hydrogen and, with a known approximation, the surface area of the catalyst.

The experiments were carried out in 50% ethanol and in 0.1 N KOH in 50% ethanol at 20 and 40°. The skeletal nickel catalyst was used only freshly prepared.

The apparatus used in the work made it possible to hydrogenate acetylene by means of sorbed hydrogen in a flow system, with simultaneous measurement of the potential of the catalyst powder [2]. The catalyst in a duck-shaped vessel, in the corresponding solvent, was saturated with hydrogen until a constant potential was reached under vigorous stirring (700-800 double swings per minute).

Fig. 1. Charging curves under anodic polarization by acetylene. 1—Pd/$CaCO_3$ (0.025 g Pd), 50% ethanol; 2—the same, 0.1 N KOH in 50% ethanol; 3—skeletal Ni (0.09 g), 50% ethanol; 4—the same, 0.1 N KOH in 50% ethanol; 5—Pt black (0.086 g), 50% ethanol.

Then the hydrogen was displaced from the duck-shaped vessel by a stream of argon, shaking was started, and 1% acetylene in argon was fed into the vessel at a constant rate. The catalyst potential was measured every minute.

The acetylene feed rate, 0.005-0.010 ml/min for Ni and 0.015-0.025 ml/min for Pd/$CaCO_3$ and Pt, ensured removal of hydrogen under equilibrium conditions ($H_{\text{ads}} \rightleftarrows H_{\text{soln}}$).

Figure 1 shows the charging curves for skeletal Ni, Pd/$CaCO_3$, and Pt black in 50% ethanol and 0.1 N KOH in 50% ethanol at 40°. In the first minute, the potential of the Ni and Pd catalysts shifts by 35-50 mV into the anodic region and remains constant until complete extraction of the occluded hydrogen. It then shifts rather rapidly to 0.35-0.40 V. On Pt there is no region of constant potential. A slow, uniform shift of the potential to $\Delta E = 0.22–0.25$ V is observed, then a rapid rise of the curve to $\Delta E = 0.37$ V; from 0.37 to 0.42 V the shift of the catalyst potential again slows down, after which it remains constant.

In each experiment, toward the end of the horizontal segment of the line, a gas sample was taken and analyzed chromatographically. Acetylene is hydrogenated quantitatively to ethane. Ethylene and acetylene were absent in all samples. The amount of ethane corresponded to the acetylene introduced.

In addition, on Pd/$CaCO_3$ and Pt black the amount of hydrogen consumed in sorption during reduction and saturation of the catalyst was compared with the amount of hydrogen removed, obtained from the charging curves. If, on the curve, one distinguishes segments *a*, *b*, and also the segment of dissolved hydrogen, then the sum of the hydrogen on them in an alcoholic medium will exactly correspond to the amount of hydrogen measured with the burette during saturation of the catalyst (after subtracting the hydrogen used for reduction of the metal).

Table 1

Amount of hydrogen extracted by acetylene from skeletal Ni, Pd/$CaCO_3$, and Pt

Solvent	T_{work}, °C	Removed hydrogen, deep	Removed hydrogen, adsorbed	Removed hydrogen, total	*S* by acetylene (m^2/g catalyst)
Skeletal nickel					
50% ethanol	20	89	18	107	39
Same	40	94	15	109	34
0.1 *N* KOH in 50% ethanol	20	113	36	149	77

Solvent	T_{work}, °C	Removed hydrogen, deep	Removed hydrogen, adsorbed	Removed hydrogen, total	S by acetylene (m^2/g catalyst)
Same	40	129	27	156	58
$Pd/CaCO_3$ (5% Pd)					
50% ethanol	20	48	80	128	8.6
Same	40	40	56	96	6.1
0.1 *N* KOH in 50% ethanol	20	72	88	160	9.5
Same	40	72	100	172	11.2
Pt black (from PtO_2)					
50% ethanol	40	–	53		

The amount of hydrogen extracted by acetylene from skeletal Ni, $Pd/CaCO_3$, and Pt, as well as the catalyst surface areas calculated from acetylene on segment *a*, are given in Table 1. The area occupied by one acetylene molecule was taken as $16 \cdot 10^{-16}$ cm^2. The total amount of hydrogen on skeletal nickel under different conditions is 107-156 cm^3/g Ni, on $Pd/CaCO_3$ 128-172 cm^3/g Pd, and on Pt 53 cm^3/g Pt. The catalyst surface area is, respectively, 34-77, 172-224, and 135 m^2/g. To confirm that the amount of hydrogen obtained in skeletal nickel cannot be overestimated due to the nickel oxidation reaction (3), we carried out the following experiments.

Charging curves were recorded on skeletal nickel in 50% ethanol and in absolute ethanol. In the experiment with absolute ethanol, every possible precaution was taken to avoid the presence of traces of water: the acetylene and hydrogen were dried, and the catalyst, after washing with water, was washed many times with absolute alcohol. The results of these experiments are shown in Fig. 2. The curves have an identical course and almost identical quantitative and qualitative characteristics with respect to hydrogen.

If nickel oxidation is assumed, the latter should sharply change its activity after the charging curve is recorded. In all media, on skeletal Ni, we carried out a series of experiments in the following sequence: after saturation of the catalyst, dimethylethynylcarbinol was hydrogenated (the potential at the end

Figure 2

Figure 2: Figure 2

of hydrogenation returns to the initial saturation potential); then the hydrogen was removed with argon, the charging curve was recorded, and then, after saturation of the catalyst with hydrogen, a repeated

Fig. 2. Charging curves recorded on $\mathrm{Ni}_{\mathrm{skel}}$ (0.09 g) at 20°. 1 –50% ethanol, 2 –absolute ethanol.

hydrogenation of dimethylethynylcarbinol. The course of the kinetic and potential curves is shown in Fig. 3. It follows from Fig. 3 that the activity of the catalyst practically does not change.

Fig. 3. Hydrogenation of dimethylethynylcarbinol in 0.1 N KOH in 50% ethanol at 20° on skeletal nickel. 1 –before recording the charging curve; 2 –after recording the charging curve.

This work confirmed our assumptions that charging curves can be recorded not only with quinone, which has a high oxidation-reduction potential, but also with compounds of the acetylene type.

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