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Abstract

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DEPENDENCE OF THE AMOUNT OF HYDROGEN ADSORBED ON SKELETAL NICKEL AND PLATINUM CATALYSTS ON THE MEDIUM

One of the necessary stages of catalytic hydrogenation is the preliminary activation of the reaction components on the surface of the catalyst. The activation of hydrogen and of the unsaturated compound on the catalyst surface depends on the specific properties of the compounds being hydrogenated, on the nature of the catalyst, and on the conditions under which the reaction is carried out: temperature, hydrogen pressure in the gas phase, stirring rate, and the medium in which the reaction is conducted. A change in the medium has a profound influence on the strength of the bond of hydrogen with the surface. By using one or another solvent, it is possible to strengthen the bond of hydrogen with the surface and thereby to change the amount of hydrogen adsorbed on the surface of the catalyst ([1],[2]).

In the present work the influence of various concentrations of alkali and acid on the adsorption of hydrogen by skeletal nickel and platinum catalysts during the hydrogenation of certain organic compounds with sorbed hydrogen was studied. Sodium maleate and *o*-nitrophenol were used as the compounds to be hydrogenated. The skeletal nickel catalyst was prepared by leaching a nickel-aluminum alloy. The platinum catalyst was prepared in the form of platinum oxide ([3]). The experiments on skeletal nickel were carried out in an aqueous NaOH solution, the concentration of which was varied from 0.01 to 15.0 N; on platinum—in aqueous solutions of NaOH and H_2SO_4. The temperature of the experiments was varied from 20 to 60°. A weighed portion of catalyst (in the case of skeletal nickel, 1 g of nickel; in the case of platinum, 0.2 g of platinum oxide) was transferred to a duck-shaped vessel and saturated with hydrogen in the corresponding medium for 1 hour. Then the hydrogen was removed from the gas phase of the vessel by a stream of nitrogen, and the substance to be hydrogenated was introduced into the vessel. With vigorous shaking of the vessel, the substance was hydrogenated with sorbed hydrogen. During the reaction the potential of the catalyst relative to a reversible hydrogen electrode was measured ([4]). After a definite time the shaker was stopped and samples of the substance were taken in a stream of nitrogen to determine the amount of hydrogen extracted from the catalyst up to that moment. The analysis was carried out by dehydrogenating the samples on a platinum catalyst.

Table 1

Amount of hydrogen (in ml) extracted by sodium maleate in 2 hours from 1 g of skeletal nickel catalyst

Temperature, °C	Alkali concentration, N	Alkali concentration, N	Alkali concentration, N	Alkali concentration, N	Alkali concentration, N	Alkali concentration, N
	0.01	0.05	0.1	0.5	1.0	5.0
20	67.4	68.4	60.3	–	36.5	25.8
40	73.1	68.3	62.5	57.9	55.5	45.4
60	77.9	69.1	65.7	60.2	58.0	52.3

The results of experiments on the hydrogenation of sodium maleate with hydrogen sorbed by a skeletal nickel catalyst are given in Table 1.

As can be seen from the table, the amount of hydrogen extracted in 2 hours decreases with increasing alkali concentration; the maximum amount of so—

is 70–80 ml. It is known that 1 g of skeletal nickel catalyst contains up to 110–120 ml of sorbed hydrogen ([2]). Consequently, sodium maleate extracts not all the sorbed hydrogen, since it is a substance with a comparatively low adsorption potential and is capable, probably, of extracting only those hydrogen atoms that are relatively weakly bound to the surface of the catalyst. Here the nature of the compound being hydrogenated has an effect ([2,5]). The maximum fall in the potential of the catalyst during hydrogenation of sodium maleate is 130–150 mV; this indicates that considerable quantities of sorbed hydrogen still remain on the surface. In accordance with this, with an increase in temperature the amount of hydrogen extracted increases, while with an increase in alkali concentration, as a result of strengthening of the bond of hydrogen with the surface, extraction of hydrogen becomes more difficult.

Fig. 1. Kinetic and potential curves for the hydrogenation of *o*-nitrophenol by hydrogen sorbed by a Ni-skeletal catalyst at various alkali concentrations. Experimental temperature 60°

To determine the dependence of the amount of sorbed hydrogen on the alkali concentration, it was necessary to choose a substance that could extract all the hydrogen sorbed by the catalyst. *o*-Nitrophenol was taken as such a substance. The results of experiments under conditions analogous to those of the preceding experiments are presented in Table 2.

Table 2

Fig. 2. Kinetic and potential curves for the hydrogenation of o-nitrophenol by hydrogen sorbed on a Ni skeletal catalyst, in 0.5 N NaOH at experimental temperatures of 20, 40, and 60°

Figure 1: Fig. 2. Kinetic and potential curves for the hydrogenation of o-nitrophenol by hydrogen sorbed on a Ni skeletal catalyst, in 0.5 N NaOH at experimental temperatures of 20, 40, and 60°

Amount of hydrogen (in ml) extracted by *o*-nitrophenol in 2 hours from 1 g of skeletal nickel catalyst.

Temperature, °C	0.01	0.05	0.1	0.5	1.0	5.0	10.0	15.0
20	105.7	107.0	113.2	113.6	113.7	125.2	–	–
40	115.2	118.9	123.6	125.3	125.6	135.0	–	–
60	127.4	132.8	136.6	137.3	137.7	148.5	160.6	–
80	–	–	–	–	–	–	164.4	–
Reversible hydrogen potential (*E* mV)	998	1050	1070	1110	1123	1150	1176	1198

Alkali concentration, N

As can be seen from Table 2, the amount of hydrogen extracted increases with increasing alkali concentration. At 60° the amount of extracted hydrogen increases from 127 ml of hydrogen in a 0.01 N solution to 160 ml in a 10.0 N alkali solution.

Figure 1 presents the kinetic and potential curves for the hydrogenation of o-nitrophenol with sorbed hydrogen at different alkali concentrations at an experimental temperature of 60°. The abscissa gives the time of hydrogen evolution; the ordinate gives the amount of hydrogen evolved and (E)—the drop in the catalyst potential from the reversible hydrogen potential. As can be seen from the figure, upon addition of o-nitrophenol the catalyst potential drops sharply in the very first minute. The higher the alkali concentration, the

Fig. 2. Kinetic and potential curves for the hydrogenation of o-nitrophenol by hydrogen sorbed on a Ni skeletal catalyst, in 0.5 N NaOH at experimental temperatures of 20, 40, and 60°

smaller the drop in the catalyst potential. In 10.0 N alkali the potential drop is 160 mV, while in 0.01 N it is more than 350 mV. In the first minute the rate of hydrogen evolution is greatest. For example, in 0.01 N alkali, 77 ml of hydrogen are evolved in the first minute, and after 2 hours of hydrogenation, 127 ml. Thus, more than half of all the evolved hydrogen is removed in the first minute.

Table 3

Acid conc., N	H_2 evolved, ml	(E), mV	Acid conc., N	H_2 evolved, ml	(E), mV
0.1	10.2	260	0.1	8.0	298
0.5	8.2	265	1.0	8.2	280
1.0	9.9	250	5.0	10.2	306
5.0	4.7	342	–	–	–

The amount of hydrogen evolved also increases with increasing temperature (see Table 2 and Fig. 2), probably at the expense of the deeper layers of the catalyst. In contrast to nickel, on a platinum catalyst the amount of adsorbed hydrogen depends almost not at all on the alkali concentration.

The results obtained for the evolution of hydrogen from 0.2 g of PtO_2 by o-nitrophenol are presented in Table 3 (experimental temperature 20°).

As can be seen from Table 3, at all concentrations of alkali and acid (except 5.0 N NaOH), approximately the same amount of hydrogen is evolved from this weighed portion of platinum oxide. This is apparently explained by the considerable bond energy of hydrogen with the surface and by the insignificant amount of hydrogen dissolved in platinum.

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