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1957

SovietRxiv

Abstract

Full Text

Physical Chemistry

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Dependence of the Catalytic Activity of Skeletal Nickel on the Conditions of Hydrogen Activation

The catalytic properties of skeletal nickel are determined by the presence in it of sorbed hydrogen. A change in the amount, as well as in the state, of this hydrogen entails a change in the activity of the contact ([1]).

The aim of the present work was to study the influence of preliminary dehydrogenation of a skeletal nickel catalyst on the rate of hydrogenation on it of dimethylethynylcarbinol in various media (0.1 N NaOH, water, 96% ethyl alcohol) and at various temperatures (20, 40, and 60°).

The catalyst (1.55 g), prepared by leaching a 31% nickel–aluminum alloy and thoroughly washed without access of air, was placed in a duck-shaped vessel with 30 ml of the working solution, where it was saturated with hydrogen for 1 hour with shaking in order to attain a standard state. Three experiments in succession were carried out on one and the same catalyst sample:

Table 1

Influence of preliminary dehydrogenation of a skeletal nickel catalyst on its activity in the hydrogenation of dimethylethynylcarbinol
(amount of catalyst 1.55 g, amount of dimethylethynylcarbinol 0.2 ml (0.1722 g))

Medium	Temperature, °C	Amount of pure hydrogen, ml	Amount of hydrogen consumed for saturation, ml	$\Delta v_0/\Delta t^*$, ml/min	$\Delta v_0'/\Delta t^*$, ml/min	Change in rate, ml	% change in rate
0.1N NaOH	20	23	23	26.0	9.6	16.4	63
0.1N NaOH	20	46	46	26.0	9.6	16.4	63
0.1N NaOH	20	85	80	26.0	9.3	16.4	63
0.1N NaOH	40	23	23	32.0	21.0	11.0	34
0.1N NaOH	40	46	46	32.0	20.0	11.0	34

Medium	Temperature, °C	Amount of pure hydrogen, ml	Amount of hydrogen consumed for saturation, ml	$\Delta v_0/\Delta t^*$, ml/min	$\Delta v_0'/\Delta t^*$, ml/min	Change in rate, ml	% change in rate
0.1*N* NaOH	40	94	79	32.0	22.0	11.0	34
0.1*N* NaOH	60	23	22	36.0	34.0	2.0	5.5
0.1*N* NaOH	60	46	34	36.0	34.0	2.0	5.5
0.1*N* NaOH	60	101	81	36.0	36.0	2.0	5.5
Water	20	23	23	31.5	21.0	10.5	33
Water	20	46	44	31.5	20.0	10.5	33
Water	20	72	66	31.5	21.0	10.5	33
Water	40	23	18	35.0	27.5	7.5	21
Water	40	46	40	35.0	27.5	7.5	21
Water	40	85	77	35.0	27.5	7.5	21
Water	60	23	23	53.0	–	3.0	6
Water	60	46	26	53.0	50.0	3.0	6
Water	60	92	77	53.0	50.0	3.0	6
96% ethyl alcohol	20	23	17.6	72.0	72.7		
96% ethyl alcohol	20	46	40.0	72.0	72.0		
96% ethyl alcohol	20	64	54.0	72.0	71.6		

* $\Delta v_0/\Delta t$ and $\Delta v_0'/\Delta t$ are the maximum reaction rates, respectively, for the fresh and the dehydrogenated catalyst.

1. The activity of a freshly prepared sample was determined by hydrogenating 0.2 ml of dimethylethynylcarbinol. In this process, the volume of hydrogen entering into the reaction was measured and, at the same time, the change in the potential of the catalyst relative to the reversible hydrogen electrode was recorded.

2. After completion of the reaction, hydrogen was removed from the gas phase of the duck-shaped vessel by a stream of nitrogen without shak-

Figure 1

Figure 1: Figure 1

ing. A calculated amount of dimethylethynylcarbinol was introduced into the duck-shaped vessel; when shaken for 30 min., this removed from the catalyst a definite, preassigned amount of sorbed hydrogen. Then, after changing the working solution and washing, the catalyst was saturated with hydrogen from the gas phase until gas absorption ceased and the value of the reversible hydrogen potential was reached.

Fig. 1. Effect of preliminary dehydrogenation of skeletal nickel on its activity in the hydrogenation of dimethylethynylcarbinol in an alkaline medium: **I** – hydrogenation on a freshly prepared catalyst; **II** –hydrogenation on the catalyst after removal of 23 ml of sorbed hydrogen; **III** –hydrogenation after removal from the catalyst of 46 ml of hydrogen; **IV** –hydrogenation after removal from the catalyst of all hydrogen reactive toward dimethylethynylcarbinol.

3. By hydrogenating 0.2 ml of dimethylethynylcarbinol on a hydrogen-saturated catalyst, the change in its activity as a result of dehydrogenation was determined.

For each medium and each temperature, the catalyst samples were subjected to successively increasing dehydrogenation, which amounted to: 23 ml of hydrogen for catalyst I, 46 ml of hydrogen for catalyst II. From catalyst III all the hydrogen reactive under the given conditions was removed; its amount was determined on the basis of the kinetic curves for hydrogenation of dimethylethynylcarbinol in a nitrogen atmosphere at the expense of sorbed hydrogen (^{2}).

The results of experiments on the hydrogenation of dimethylethynylcarbinol on dehydrogenated skeletal nickel are given in Table 1 and in Fig. 1 for the alkaline medium, respectively at temperatures of 20, 40, and 60°. The kinetic curves in the upper half of the graphs represent the rate of hydrogenation of 0.2 ml of the acetylenic alcohol; the lower curves show the change in the catalyst potential in the course of the reaction. Similar curves were obtained for experiments in aqueous and alcoholic media.

From Fig. 1 and Table 1 it is seen that, depending on the medium and temperature, preliminary removal from the catalyst surface of part or all of the sorbed ...

dehydrated hydrogen affects the catalytic activity of nickel in different ways. Especially large changes in the reaction rate as a result of dehydrogenation occur during hydrogenation in an alkaline medium at low temperatures. Thus, at 20°, removal of 23 ml of hydrogen from the catalyst surface causes its activity to decrease by 63%; with an increase in temperature to 40°, the decrease in the reaction rate as a result of removal of 23 ml of hydrogen is 34%, while at 60° under the same conditions dehydrogenation has almost no effect on the

operation of the contact.

In an aqueous medium, skeletal nickel proves less sensitive to dehydrogenation. At 20° the rate of hydrogenation of 0.2 ml of dimethylethynylcarbinol after removal of 23 ml of hydrogen from the surface decreases by 33%, at 40° by 21%, and at 60° by 6%. It is interesting to note that a subsequent increase in the degree of dehydrogenation in alkali and in water no longer produces any further change in the activity of the catalyst.

In an alcoholic medium, removal from the surface of all the hydrogen that is reactive with respect to dimethylethynylcarbinol has absolutely no effect on the rate of the hydrogenation process.

The results obtained can be explained by the different rates of activation of hydrogen on the dehydrogenated catalyst, depending on the medium and the temperature. In an alkaline medium, where hydrogen is very firmly bound to the surface, its renewal proceeds with great difficulty and at a low rate, which is expressed in a 63% decrease in the reaction rate, despite the fact that, when the catalyst is saturated from the gas phase, the amount of hydrogen lost is completely absorbed. In an aqueous medium, activation of hydrogen proceeds faster and more readily; therefore the dehydrogenation process affects the rate to a lesser extent. In an alcoholic medium, where the bond of hydrogen with the catalyst surface is insignificant, easy renewal of activated hydrogen ensures a stable working state of skeletal nickel.

Since increasing the temperature of the experiment has a favorable effect on the process of hydrogen activation, dehydrogenation at 40 and 60° does not substantially reduce the reaction rate.

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Received
18 II 1957

CITED LITERATURE

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