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Abstract

Full Text

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ON THE CHEMICAL NONEQUIVALENCE OF ACTIVE HYDROGEN SORBED BY A SKELETAL NICKEL CATALYST

The chemical nonequivalence of hydrogen sorbed by a skeletal nickel catalyst was observed by L. Kh. Freidlin ([1,2]) and D. V. Sokol' skii ([3,4]) and their co-workers during liquid-phase hydrogenation of unsaturated compounds of various classes. On the basis of these observations the authors concluded that on a skeletal nickel catalyst there are two forms of active hydrogen: surface-adsorbed and dissolved. Surface-adsorbed hydrogen is bound to nickel more weakly than dissolved hydrogen, is removed from the catalyst by unsaturated compounds first of all, and its loss is readily compensated by hydrogen from the gas phase. Dissolved hydrogen forms part of the active centers of the catalyst, and its removal from the catalyst leads to deactivation of the latter.

We were able to observe the different action of different forms of active hydrogen sorbed by a skeletal nickel catalyst in studying the reaction of double-bond migration in 1-hexene under conditions of its incomplete hydrogenation in ethyl alcohol solution at room temperature. It is known that the reaction of double-bond migration in olefins in the presence of hydrogenation catalysts proceeds only in the presence of hydrogen; to elucidate the role of different forms of hydrogen we carried out experiments with 1-hexene under the following conditions: a) with introduction from outside of the entire amount of hydrogen capable of adding to hexene during the experiment; b) with introduction of a limited amount of hydrogen during the same interval of time; and c) without introduction of hydrogen from outside. In each experiment fresh portions of catalyst were taken. Experiments Nos. 1–11 were carried out with one catalyst sample, and experiments Nos. 12–16 with another, less active one. The catalyzates were analyzed by gas–liquid chromatography and, in addition to the initial 1-hexene, contained *n*-hexane and a mixture of cis- and trans-2-hexenes. The conditions for carrying out the experiments and their results are given in Table 1.

Table 1

Experiment Nos.	Catalyst sample	Charge of 1-hexene, g	Charge of nickel, g	Conditions of hydrogen supply	Duration of experiment, min	Hydrogenation, %	Isomerization, %
1	I	0.33	0.6303	a	3	18.2	16.5
2	I	0.33	0.6304	b	3	13.0	14.6
3	I	0.33	0.6305	b	3	12.8	14.5
4	I	0.33	0.6303	b	3	8.5	13.9
5	I	0.33	0.6300	c	3	2.0	12.8
6	I	0.33	1.1554	a	3	26.4	34.5
7	I	0.33	1.1560	b	3	19.4	29.0
8	I	0.33	1.1553	b	3	17.0	28.5
9	I	0.33	1.1568	b	3	14.0	27.6
10	I	0.33	1.1555	b	3	9.0	25.7
11	I	0.33	1.1568	c	3	4.0	24.5
12	II	0.33	1.1124	a	20	26	7.5
13	II	0.33	1.1127	b	20	24	8.0
14	II	0.33	1.1110	b	20	9	8.0
15	II	0.33	1.1117	b	20	3	8.0
16	II	0.33	1.1122	c	20	1–1.5	8.0

It follows from the data in Table 1 that, with a limited supply of hydrogen, under conditions of "hydrogen starvation" of the catalyst, the content of isomerization products in the catalyzates depended very little on the amount of hydrogen supplied from outside, and depended practically on the amount of hydrogen contained in the catalyst (the amount of hydrogen contained in a given weighed portion of catalyst can be judged from the hydrogenation reaction of hexene-1 in experiments without supplying hydrogen from outside).

The results obtained may be interpreted as follows. Hydrogenation of hexene-1 occurs predominantly at the expense of surface-adsorbed hydrogen, the amount of which is determined by the amount of hydrogen supplied from outside, whereas isomerization of hexene-1 occurs predominantly at the expense of hydrogen dissolved in nickel. Such hydrogen, as is known, is present in metals in the form of atoms or protons (5), while that present on the surface of the metal is present in the form of molecules, partially activated. Apparently, hydrogenation of the olefin and migration of the double bond in it proceed by different mechanisms, which will be formulated later, after a more detailed experimental study of these reactions on various catalysts.

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