INVESTIGATION OF DEUTERIUM—HYDROGEN EXCHANGE OF CYCLIC HYDROCARBONS ON METALLIC CATALYSTS
COMMUNICATION 1. PRINCIPLES OF DEUTERIUM—HYDROGEN EXCHANGE OF CYCLOHEXANE ON NICKEL CATALYSTS

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The investigation of the isotopic exchange of hydrocarbons with deuterium has yielded valuable information on the mechanism of processes of hydrogenation, dehydrogenation, and isomerization [1-5]. The distribution of deuterium in the products, which varies with time and depends on the specific conditions of the process, reflects the complex nature of isotopic exchange in hydrocarbons. Evidently it is determined by the simultaneous occurrence of the reaction along different pathways at different rates, which also leads to different rates of accumulation of various products of exchange. An investigation of the change in the distribution of deuterium in the products during exchange can give new information on the mechanism of the interaction of hydrocarbons with catalytic surfaces and on the reactivity of the surface compounds.

The purpose of this work was to study the isotopic exchange of hydrogen with deuterium in cyclic hydrocarbons on various metallic catalysts. This communication presents the results of a study of the general principles of the reaction of isotopic exchange in cyclohexane on nickel catalysts, necessary for a further precise kinetic investigation.

EXPERIMENTAL

The reaction of isotopic exchange

\[ C_6H_{12} + n/2D_2 = C_6H_{12-n}D_n + n/2H_2 \]  

\( 0 \leq n \leq 12 \) was studied in a static vacuum circulation system, connected to an MI-1305 mass spectrometer. The apparatus did not contain mercury vapors; the possibility of the penetration of vapors of the vacuum grease to the catalyst was minimized by using metallic vacuum stopcocks in the reaction portion. The reactor was a cylindrical vessel with porous partition, above which the catalyst was held between layers of broken glass. The reactor was equipped with a coil for preliminary preheating of the reaction mixture. The pressure of the gases was determined with a standard mercuryless vacuum gauge. The rate of circulation was \(~150\) liters/h, which practically eliminated the possibility of the inhibition of the reaction on account of external diffusion under conditions of reduced pressure.

At 5 or 10 min intervals, the reaction mixture continuously passing through the feed valve into the mass spectrometer was analyzed. This did not cause any appreciable reduction of the pressure in the reaction volume during the experiment. Mass spectral analysis was conducted at an ionizing voltage of 20 V; in the calculations a correction is introduced for the natural content of heavy isotopes of carbon and hydrogen.

The catalyst Ni/Al₂O₃ (C-I) was produced by the method of gas phase application. The content of Ni was 3.8%, surface of the active phase 6.6 m²/g. Before the experiment, a weighed sample of the catalyst (1.3 g) was reduced with deuterium directly in the reactor in a circulation system for 6 h at 350°, repeating this operation three times and evacuating the system to a residual pressure of 10⁻⁵ mm Hg.

Fig. 1. Dependence of the concentration of certain products of isotopic exchange and the value of $MD$ on the time of the experiment: 1) $MD$; 2) concentration of cyclohexane $d_1$; 3) $d_2$; 4) $d_{11}$; 5) $d_{12}$ (catalyst Ni/Al$_2$O$_3$, $p$$_2$ 25 mm Hg, $D_2$ : C$_6$H$_{12}$ = 60 : 1, 30$^\circ$).

Fig. 2. Dependence of the ratio $d_{12}/d_1$ on the conditions of treatment of the catalyst Ni/Al$_2$O$_3$ ($p$$_2$ 25 mm, $D_2$ : C$_6$H$_{12}$ = 60 : 1, 30$^\circ$): 1) evacuation of catalyst before the experiment at 440$^\circ$ to a pressure of 2 - 3 $\cdot$ $10^{-6}$ mm; 2) the same at 200$^\circ$; 3) treatment of the catalyst with deuterium at 50 mm in a circulation system at 300$^\circ$ for 2 h, evacuation at 300$^\circ$ to a pressure of 2 - 3 $\cdot$ $10^{-6}$ mm; 4) treatment with deuterium at 400$^\circ$, evacuation at 30$^\circ$.

Fig. 3. Variation of the concentration of cyclohexane $d_1$ and $d_{12}$ as a function of the activity of the catalyst Ni/Al$_2$O$_3$: 1) degree of exchange $x$; 2) concentration of cyclohexane $d_1$; 3) concentration of cyclohexane $d_{12}$ ($p$$_2$ 25 mm, $D_2$ : C$_6$H$_{12}$ = 60 : 1, 30$^\circ$, 30 min).

The Ni/ZnO catalyst (C-II) was prepared according to the method of [6]. The Ni content was 25%, surface of nickel 4.6 m$^2$/g. The weight of the sample for each experiment was 1.6 g. Reduction was conducted according to the method described above.

Grade cp cyclohexane was purified on a preparative chromatograph, and before introduction into the apparatus was freed of dissolved gases by three repeated operations of freezing (liquid nitrogen)—evacuation—thawing, and was sealed under vacuum into a special ampule, easily broken with a small magnet. Deuterium (98% pure) was purified by passing through a Pd capillary. The initial reaction mixture, with minimum ratio $p$$_D_2$ : $p$$_C_6H_{12}$ = 5 : 1 usable in the experiments, was prepared by breaking the ampule with cyclohexane in a cylinder filled with the corresponding amount of deuterium. To obtain a mixture with a larger ratio $p$$_D_2$ : $p$$_C_6H_{12}$, the required amount of deuterium was added to the initial mixture in a definite volume before passage into the reactor.

The experiments on the catalyst C-I were conducted at 30$^\circ$, those on the catalyst C-II at 50$^\circ$; the pressure of the reaction mixture was from 10 to 320 mm at ratios of the initial partial pressures $p$$_D_2$ : $p$$_C_6H_{12}$ from 5 : 1 to 100 : 1. The rate of accumulation of various deuterocyclohexanes was determined graphically, according to the initial slope of the accumulation curves.

DISCUSSION OF RESULTS

One of the basic difficulties that must be encountered in the study of the kinetics of heterogeneous catalytic reactions is the inconstancy of the activity of the catalyst. In the isotopic exchange of hydrocarbons with deuterium, an additional difficulty arises: experience shows that even with the same degree of exchange $x$, estimated according to the decrease in nondeuterated cyclohexane, the ratio between products of different degrees of deuteration (degree of exchange) may be substantially different:

$$x = \left( \frac{\sum_{n=1}^{12} d_n}{\sum_{n=0}^{12} d_n} \right) \cdot 100$$

($d_n$ is the fraction of cyclohexane containing $n$ deuterium atoms in the molecule; 0 $\leq n \leq$ 12). The degree of exchange is usually estimated by the quantity $MD$, calculated according to Kemball's formula [7]:

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