INVESTIGATION OF THE KINETICS OF THE ISOMERIZATION
OF n-PENTANE ON THE HYDROGEN FORM OF MORDENITE
AT LOW PARTIAL PRESSURES OF HYDROGEN

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It was shown earlier [1] that the isomerization of n-pentane on the H-form of mordenite without metals of group VIII is inhibited by H₂ in the range of pressures 7-30 atm. However, it is known [2] that without H₂ the reaction on this catalyst practically does not occur. Therefore, to determine the mechanism of the isomerization on the H-form of mordenite, it is of interest to investigate the kinetics of the reaction at low partial pressures of hydrogen (from 0 to 7-10 atm). This was the purpose of the present work. To consider the influence of deactivation of the catalyst under these conditions on the rate of the process we developed a special procedure for conducting the experiments and treating the experimental data.

METHOD

The isomerization of n-pentane was studied in a flow-through reactor, into which 10 cm³ of mordenite in the H-form with a degree of exchange of Na⁺ ions for H⁺ of 95 eq. %, was loaded. The catalyst was prepared by the method of ion exchange of Na⁺ cations in the initial Na-form for NH₄⁺, by five treatments of mordenite with a 10% solution of NH₄NO₃. Before the experiments the catalyst was treated with air at 520° for 5 h. Regeneration of the catalyst after each experiment was conducted under the same conditions. Since the catalyst works unstably at low partial pressures of hydrogen (Fig. 1) and lowers its activity to some constant level, which depends on the experimental conditions, we used the following procedure. Isomerization under the control conditions at Pₜ₀ = 30 atm; PH₂/PC₅ = 3.2, vC₅ = 1-3 h⁻¹ (depending on the temperature) was conducted on a fresh, regenerated catalyst. After this, the pressure was lowered to the set value (Pₜ₀ = 4-8 atm), and we operated in this system for 60-90 min. In this case the activity of the catalyst, as has already been noted, was lowered (see Fig. 1). Then the control experiment was repeated again. The degree of deactivation of the catalyst (γ) during work at low temperature was calculated according to the formula

$$\gamma = \frac{r_{\text{init}}}{r_{\text{fin}}}$$

where r_init is the rate of isomerization under the control conditions before the basic experiment was conducted; r_fin is the rate of the isomerization reaction under the control conditions after the basic experiment was conducted at low pressure. Considering the activation of the catalyst, we calculated the corrected reaction rate (r_corr) in the basic experiment, which would be observed in the absence of poisoning of the catalyst, according to the formula

![Fig. 1. Dependence of the yield of isopentane on the time of work of the catalyst at 200° and a partial pressure of hydrogen (pH₂) 6 atm (1) and 230° and pH₂ 2 atm (2).](image)
where $r_{\text{obs}}$ is the observable reaction rate, corresponding to the lower stable level of activity of the catalyst (see Fig. 1).

From the data obtained (Table 1) it is evident that the degree of deactivation of the catalyst varies from 3.5 to 10, depending on the conditions of isomerization.

**RESULTS AND DISCUSSION**

In order to have a general idea of the dependence of the rate of isomerization on the partial pressure of $H_2$, the data obtained in this work were compared (Figs. 2-4) with the results of our previous investigation in the region of pressures 7-30 atm [1]. As can be seen from Figs. 2-4, the observable reaction rate passes through a maximum, which lies in the region of partial pressures of hydrogen 7-10 atm.

The nature of the right-hand branches of the curves on these figures was explained in our previous communication [1] on the basis of the proposed reaction mechanism

\[ n-C_5H_{12} + HM \rightleftharpoons n-C_5H_{11} - M + H_2 \]  
\[ n-C_5H_{11} - M \rightleftharpoons i-C_5H_{11} - M \]  
\[ i-C_5H_{11} - M + H_2 \rightarrow i-C_5H_{12} + HM \]

where HM is the hydrogen form of mordenite; $n-C_5H_{11} - M$ and $i-C_5H_{11} - M$ are carbonium cations, bound to the active centers of mordenite. From the scheme presented it is evident that $H_2$ shifts the equilibrium of the first step of the reaction, in which the carbonium cation and $H_2$ molecule are formed in the interaction of a molecule of $n$-pentane with a proton of the acid hydroxyl group of mordenite. The drop in the observable reaction rate with decreasing partial pressure of hydrogen in the interval from 0 to 7-10 atm is associated with deactivation of the catalyst. The corrected rate of the isomerization reaction in this range of pressures does not depend on the partial pressure of hydrogen (see Figs. 2-4).

In our previous communication [1] we derived a kinetic equation, which for the reaction in the forward direction takes the following form

\[ r = \frac{k_a p_{n-C_5}/p_{H_2}}{1 + a p_{n-C_5}/p_{H_2}} \]  

(III)

where $a$ is the equilibrium constant of the first step; $k$ is the rate constant of isomerization of the normal carbonium cation to a cation of iso-structure. According to this equation, the rate of the reaction (r) at constant temperature depends only on the ratio of the partial pressures of $n$-pentane and $H_2$ ($p_{n-C_5}/p_{H_2}$). Moreover, at low ratios $p_{n-C_5}/p_{H_2}$, when $1 \gg a p_{n-C_5}/p_{H_2}$

\[ r = \frac{k a p_{n-C_5}/p_{H_2}}{1 + a p_{n-C_5}/p_{H_2}} \]  

(IV)

while at high $p_{n-C_5}/p_{H_2}$, when $1 \ll a p_{n-C_5}/p_{H_2}$

\[ r = k \]  

(V)