KINETICS OF THE HYDROGENATION OF 2-METHYL-2-BUTENE ON THE RUBIDIUM FORM OF TYPE-Y ZEOLITE

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It was shown earlier that alkali and alkaline-earth cationic forms of zeolite exhibit high activity in the hydrogenation of aromatic and unsaturated hydrocarbons [1-5]. Data have been cited, indicating that the catalytic activity in the hydrogenation of C_6H_6 is associated with the presence of ion-exchange cations in the zeolites [2]. In the conversions of amylenes on cationic forms of various zeolites, simultaneously with the hydrogenation of the olefins, there is an isomerization of them [4]. It has been suggested that isomerization may proceed through an intermediate semihydrogenated state, arising as a result of the successive addition of dissociatively adsorbed H_2 to the olefin molecule.

The kinetic principles of the hydrogenation of olefins on alkali and alkaline-earth forms of zeolites have been very little studied. And yet, this is essential for an understanding of the mechanism of the catalytic action of zeolites in hydrogenation reactions. In this work we investigated the kinetics of the hydrogenation of 2-methyl-2-butene (MB-2) on a Rb form of type-Y zeolite.

EXPERIMENTAL METHOD

The reaction was studied in a flow-type setup, designed for work under pressure, RbNaY zeolite with a 81% degree of exchange was used as the catalyst. The catalyst was prepared by repeated contact of NaY zeolite (SiO_2/Al_2O_3 = 4.3) with a 12% solution of RbCl. After exchange, the zeolite was washed with distilled water, dried at 100°, and pressed without binder into 3 × 3 mm tablets. The degree of exchange of Na^+ for Rb^+ was determined by the method of flame photometry. The preservation of the crystal structure of the zeolite after preparation and use in catalytic experiments was evaluated according to the adsorption capacity with respect to the N_2, determined by a chromatographic method, as well as according to the data of x-ray diffraction study. These measurements did not show any changes in the crystal structure of the catalyst.

The starting materials were electrolytic grade H_2 from a cylinder and MB-2 which contained 1.5% n-pentane and 0.7% trans-2-pentene according to the data of chromatographic analysis. The reaction was studied at 200-260°, partial pressures of MB-2 1-10 atm, H_2 5-40 atm, amount of the catalyst 0.8-2.0 g, and rate of delivery of MB-2 4.2-42.0 ml/h. For each temperature the space velocity was selected so that the yield of the products [isopentane and 2-methyl-1-butene (MB-1)] did not go beyond the region of a pseudozero order of the reaction. The reaction rate was calculated according to the equation [6]

$$r = \frac{vdX}{Mg \cdot 100} \text{ moles/g of catalyst} \cdot \text{h}, \quad (1)$$

where v is the rate of delivery of MB-2, ml/h; d is the specific gravity of the olefin, g/cm^3; X is the degree of conversion, %; M is the molecular weight of the hydrocarbon; g is the amount of the catalyst, grams. Before each experiment, the catalyst was activated in a stream of air at 500° for 5 h. Since the catalyst worked unstably, and the yield of isopentane decreased during the experiment, to find the initial rate of the hydrogenation

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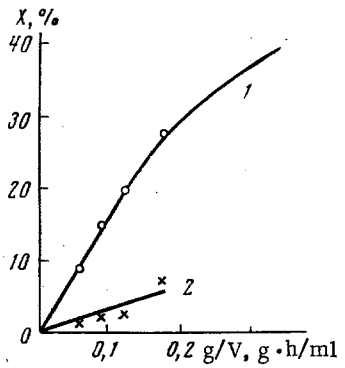

Fig. 1

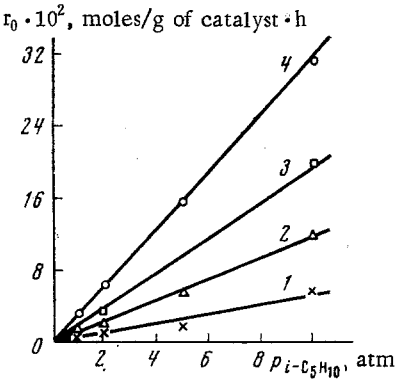

Fig. 2

Fig. 1. Dependence of the yield of isopentane (1) and 2-methyl-1-butene (2) in the hydrogenation of MB-2 on the conditional time of contact (g/v, g·h/ml) at 200°, P_{tot} = 27 atm, $p_{H_2}/p_{i\text{-}C_5H_{10}}$ = 12.5.

Fig. 2. Dependence of the rate of formation of isopentane on the partial pressure of 2-methyl-2-butene at temperatures, °C: 1) 200; 2) 220; 3) 240; 4) 260. p_{H_2} = 25 atm.

reaction r_0, an extrapolation was made according to the equation [5]

$$r = r_0 e^{-\alpha\tau}, \quad (2)$$

where α is a constant for the given experimental conditions, characterizing the rate of decrease in the activity of the catalyst; τ is the time. In [5] it was shown that r_0, determined according to Eq. (2), has a mean square error of ±8% rel.

DISCUSSION OF RESULTS

The dependence of the initial rate of conversion of MB-2 on the conditional time of contact (g/v) showed (Fig. 1) that the pseudozero order of the hydrogenation reaction is preserved up to an ~30% yield of isopentane. Therefore, the experiments were conducted under conditions in which the yield of isopentane did not exceed 30%. The yield of MB-1 was directly dependent on the conditional time of contact (see Fig. 1). In contrast to isopentane, the yield of MB-1 did not change with time during the work of the catalyst.

From the graphical dependence of the initial rate of hydrogenation of MB-2 on the partial pressures of the hydrocarbons and H_2 (Figs. 2 and 3), it is evident that r_0 is directly proportional to the partial pressures of the reagents, i.e., the reaction is first order with respect to the olefin and with respect to H_2. Consequently, the rate of hydrogenation is described by the equation

$$r = k p_{i\text{-}C_5H_{10}} p_{H_2}, \quad (3)$$

where k is the apparent rate constant of the reaction; $p_{i\text{-}C_5H_{10}}$ and p_{H_2} are the partial pressures of the components.

Calculation of the rate constant of the reaction according to Eq. (3) for various temperatures showed that k has a mean square dispersion that does not exceed 25% rel., while the apparent activation energy is 15 ± 2 kcal/mole. The temperature dependence of the reaction rate constant obeys the equation $k = 1.5 \cdot 10^3 \exp(15{,}000/RT)$.

From Fig. 4 it is evident that the rate of formation of MB-1 is directly proportional to the partial pressure of MB-2. The dependence of the rate of isomerization on the partial pressure of H_2 could not be detected in explicit form, since at relatively high yields of isopentane, the amount of MB-1 in the reaction products was reduced as a result of its hydrogenation. Moreover, the isomerization of the olefin may proceed according to two mechanisms. In [4] it was shown that most of the MB-1 is formed on acid centers of the zeolite, such as decationized portions. A certain fraction of the MB-1 is probably obtained as a result of the occurrence of the reaction through a semihydrogenated intermediate compound. The latter mechanism is confirmed by the following experimental facts. At low partial pressures of the hydrocarbon (1-2 atm), the rates of isomerization of MB-2 in the presence of H_2 and He are close (Fig. 5), but beginning with 5 atm the reaction rate

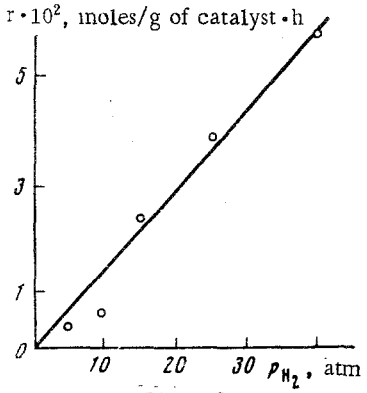

Fig. 3

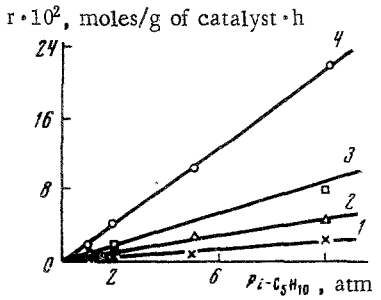

Fig. 4

Fig. 3. Dependence of the rate of formation of isopentane on the partial pressure of H_2 at 240° and partial pressure of 2-methyl-2-butene 2 atm.

Fig. 4. Dependence of the rate of migration of the double bond on the partial pressure of 2-methyl-2-butene at temperatures, °C: 1) 200; 2) 220; 3) 240; 4) 260. p_{H_2} = 25 atm.

in H_2 is higher than in He. An investigation of the influence of pyridine on the isomerization of MB-2 showed that this base, added in an amount of 3.5% to the initial hydrocarbon, almost entirely suppresses the reaction when the process is carried out under He pressure. However, MB-1 is formed when the experiment is carried out under H_2 pressure, when hydrogenation of the initial isoamylene occurs. In this case the yield of MB-1 decreases with time in proportion to the yield of isopentane (Fig. 6). These results permit us to assume that migration of the double bond in the olefin in this case occurs both on the acid portions of the surface and through a semihydrogenated intermediate state on the hydrogenating active sites of the zeolite.

Considering the aforementioned, we derived a kinetic equation of the hydrogenation reaction on the basis of the following scheme of conversion of MB-2 on the surface of the catalyst:

$$(CH_3)_2C{=}\overset{A}{C}HCH_3 + 2H \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (CH_3)_2\overset{*}{C}\overset{\overset{*}{A}}{C}H_2CH_3 + H \xrightarrow{k_3} (CH_3)_2\overset{B}{C}HCH_2CH_3$$

$$k_2 \downarrow\uparrow k_{-2}$$

$$CH_2{=}CCH_2CH_3 + H$$

$$|$$

$$CH_3$$

$$C$$

Applying the condition of quasiequilibrium for the intermediate semihydrogenated compound $d[\overset{*}{A}]/d\tau = 0$, we can determine its concentration

$$[\overset{*}{A}]' = \frac{k_1[A][H] + k_{-2}[C][H]}{2k_{-1}[\ ] + 6k_2[\ ] + k_3[H]}$$

where [ ] denotes the active sites on the surface of the catalyst. If the concentration of the imtermediate semihydrogenated compound $\overset{*}{A}$ can be neglected in comparison with the surface concentrations of the starting materials, then by applying the Langmuir isotherm for the adsorption of the starting materials and assuming that $k_1 = k_{-2} = k_{1,-2}$, while $k_{-1} = k_2 = k_{-1,2}$, we can obtain the following expression for the rate of hydrogenation:

$$r = \frac{k p_{i\text{-}C_5H_{10}} p_{H_2}}{(1 + k' p_{H_2}^{0,5})(1 + a_{i\text{-}C_5H_{10}} p_{i\text{-}C_5H_{10}} + a_{H_2}^{0,5} p_{H_2}^{0,5})^2} \qquad (5)$$

where $k = k'k_{1,-2}\, a_{i\text{-}C_5H_{10}} a_{H_2}^{0,5}$; $k' = k_3/8k_{-1,2}\, a_{H_2}^{0,5}$, a is the adsorption coefficient of the corresponding components of the reaction. In the derivation of Eq. (5) the difference between the H atoms at the primary and secondary C atoms in the intermediate semihydro-

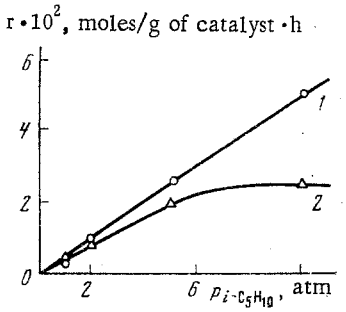

Fig. 5

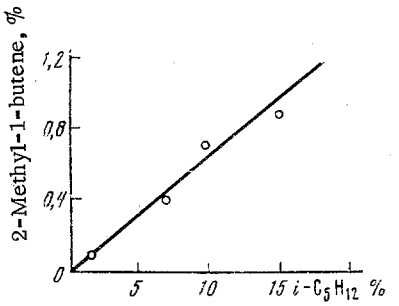

Fig. 6

Fig. 5. Dependence of the rate of migration of the double bond on the partial pressure of 2-methyl-2-butene at 220° and a partial pressure of H_2 (1) and He (2) equal to 25 atm.

Fig. 6. Dependence of the yield of 2-methyl-1-butene on the yield of isopentane at 200°. P_{tot} = 35 atm, $p_{H_2}/p_{i\text{-}C_5H_{10}}$ = 2.5. The initial 2-methyl-2-butene contains 3.5% pyridine.

genated compound was not considered. The energies of the C—H bonds at the primary and secondary C atoms are 94-101 and 93 kcal/mole, respectively [7]. The difference is inconsequential, and it can be neglected. At low values of the adsorption coefficients, i.e., when all the components in the denominator are negligible in comparison with one, Eq. (5) is converted to the empirically found equation (3), which satisfactorily describes the experimental data.

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CONCLUSIONS

1. The rate of hydrogenation of 2-methyl-2-butene on the Rb form of type Y zeolite is directly proportional to the partial pressures of the olefin and H_2.

2. The kinetic equation of the hydrogenation reaction, derived on the basis of a scheme assuming the formation of an intermediate semihydrogenated complex, well describes the experimental data obtained.

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