HYDROGENATION OF PENTYNES ON CATIONIC FORMS OF ZEOLITE Y

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The cationic forms of the zeolites are quite active in the hydrogenation of aromatic, olefinic, and dienic hydrocarbons [1-4], their catalytic activity depends on the concentration and type of cations [5, 6], and the mechanism of the reaction includes the successive addition of either hydrogen atoms or ions to unsaturated bonds [3, 4].

In order to refine the specific traits of the catalytic action of zeolites in hydrogenation reactions we studied the hydrogenation of the acetylenic hydrocarbons, 1-pentyne and 2-pentyne, on the cationic forms of a type Y zeolite.

EXPERIMENTAL

The employed flow equipment was run under pressure [3], and the 1-pentyne and 2-pentyne were 99% pure. The 2-pentyne was obtained by the isomerization of 1-pentyne in the presence of KOH and subsequent fractional distillation through a column with an efficiency of 20 theoretical plates. For reaction we took a mixture of the pentyne and n-hexane in a 1:2 ratio. The experiments were run in the range 140-220°C at 30 atm. Samples were taken at 15 min intervals during experiment, which were analyzed by the GLC method.

The amount of catalyst, charged into the reactor, was 5 ml. As catalysts we used zeolite NaY (SiO_2/Al_2O_3 = 5.0) and also the Li^+, K^+, Ca^{2+}, and La^{3+} forms of this zeolite, which were prepared by the ion exchange method [4]. Prior to experiment the catalysts were heated for 5 h in an air stream at 500°. The yield of the hydrogenation products remained constant during the time of experiment, or in some cases it decreased somewhat. The results of the first sample are given, which was taken 1 h after the start of experiment.

DISCUSSION OF RESULTS

In the hydrogenation of 2-pentyne the primary product is cis-2-pentene (Fig. 1), which corresponds to the cis addition of hydrogen to the triple bond, which is characteristic for metal catalysts [7]. It is interesting to mention that in the hydrogenation of 2-pentyne a certain amount of 1-pentene is also formed as a primary product (Fig. 2), since the 1-pentene/2-pentene ratio remains practically constant with conversion of the starting hydrocarbon. When 1-pentyne is hydrogenated on the univalent cationic forms, it is frequently isomerized to 2-pentyne. An intermediate product, namely 1,2-pentadiene, is also formed here, while the products of the hydrogenation reaction are all three n-amylene isomers.

A comparison of the hydrogenating activities of the various cationic forms of zeolite Y is given in Table 1. In calculating the specific activity of the cations we took into consideration only the cations that are located in the large cavities of the zeolite, whose amount was determined by the decationization of the sample at ∿20° [4]. The cationic forms of zeolite Y, given in Table 1, were selected in such a way that a change in the electrostatic potential e/R^2, with a constancy in the ionization potential I, occurred in one group of cations (K^+, Na^+, Li^+), and a change in the higher ionization potential, with a constancy in the electrostatic potential, occurred in the other group (Li^+, Ca^{2+}, La^{3+}). A comparison of the given series of cations permits determining which property is responsible for the catalytic activity. In other cases this problem is difficult to solve due to the correlation of the properties of the cations [4]. As can be seen from the obtained data, the specific hydrogenating activity of the zeolite is determined by the higher ionization potential of the cation and is independent of its electrostatic potential. An analogous conclusion was made previously when studying the hydrogenation of piperylene on zeolites [4].

From Table 1 it can be seen that close hydrogenation rates for 1-pentyne are achieved at a higher temperature than for 2-pentyne. The reasons for this are not entirely clear. It is possible that 1-pentyne reacts more strongly with the basic centers of the zeolite, which hinders its hydrogenation.

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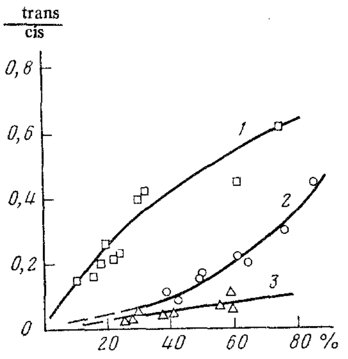

Fig. 1

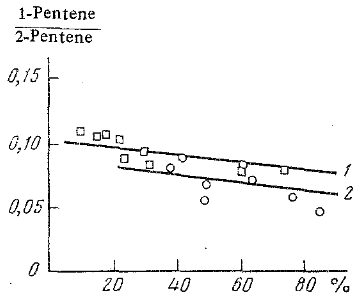

Fig. 2

Fig. 1. trans-2-Pentene/cis-2-pentene ratio as a function of the degree of hydrogenation of piperylene: 1) 0.73LiY; 2) NaY; 3) 0.70KY.

Fig. 2. 1-Pentene/2-pentene ratio as a function of the degree of hydrogenation of piperylene: 1) 0.73LiY; 2) NaY.

TABLE 1. Hydrogenating Activity of Zeolite Y as a Function of Properties of Cations (P_{H_2} = 24 atm, $P_{C_5H_8}$ = 3 atm, v = 1 h^{-1})

Zeolite	I, V	e/R^2	Hydrogenation of 2-pentyne at 180°		Hydrogenation of 1-pentyne at 240°	
			$r_{total}\cdot10^4$, mole/g cat·h	r_{sp}, mole/g·ion·h	$r_{total}\cdot10^4$, mole/g cat·h	r_{sp}, mole/g·ion·h
0,70KY	4,34	0,56	36,20	1,12	24,46	0,75
NaY	5,14	1,04	22,28	0,69	21,08	0,65
0,73LiY	5,39	2,16	30,63	0,94	14,74	0,46
0,85CaY	11,87	1,85	17,07	1,51	21,94	1,94
0,62LaY	19,17	2,00	22,72	3,85	28,71	4,87

CONCLUSIONS

1. The cis addition of hydrogen to the triple bond occurs when 2-pentyne is hydrogenated.

2. The specific activity of a zeolite in the hydrogenation of pentynes is determined by the higher ionization potential of the cation.

LITERATURE CITED

1. Kh. M. Minachev, V. I. Garanin, V. V. Kharlamov, and T. A. Isakova, Kinet. Katal., 13, 1101 (1972).
2. V. V. Kharlamov, V. I. Garanin, D. B. Tagiev, Kh. M. Minachev, and A. A. Goryachev, Izv. Akad. Nauk SSSR, Ser. Khim., 1975, 673.
3. Kh. M. Minachev, V. V. Kharlamov, and N. G. Kharatishvili, Izv. Akad Nauk SSSR, Ser. Khim., 1979, 97.
4. V. V. Kharlamov, N. G. Kharatishvili, Yu. A. Borisov, P. I. Slyunyaev, and Kh. M. Minachev, Izv. Akad. Nauk SSSR, Ser. Khim., 1980, 1497.
5. Kh. M. Minachev, V. V. Kharlamov, V. I. Garanin, and D. B. Tagiev, Izv. Akad. Nauk SSSR, Ser. Khim., 1976, 1709.
6. Kh. M. Minachev, V. I. Garanin, V. V. Kharlamov, and M. A. Kapustin, Izv. Akad. Nauk SSSR, Ser. Khim., 1975, 2673.
7. J. K. Bond and P. B. Wells, Catalysis. Physical Chemistry of Heterogeneous Catalysis [Russian translation], Mir, Moscow (1967), p. 351.