CONCLUSIONS

1. A new procedure for the experimental testing of the theory of capillary gas chromatography is proposed.

2. The difference between experiment and Golay's theory due to resistance to mass transfer at the gas—liquid boundary amounts to 23% of the observed height equivalent to a theoretical plate.

3. Taking the finite thickness of the interphase layer and its special absorption properties into account leads to a quadratic form of the dependence of the interphase resistance on the coefficient of mass transfer.

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HYDROGENATION OF PIPERYLENE ON CATIONIC FORMS

OF VARIOUS ZEOLITES

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Cationic forms of zeolites are catalytically active in the hydrogenation of various compounds [1-6]. In [5] it was shown that when piperylene is hydrogenated on Na forms of zeolites, hydrogen is added to the unsaturated bonds in the form of individual atoms or ions. The purpose of the present work was to verify this conclusion in the case of the hydrogenation of piperylene on multiply charged cationic forms of zeolites and to ascertain the property of the cations which is responsible for the hydrogenating activity of the zeolites.

EXPERIMENTAL

Piperylene was hydrogenated in a flow-type reactor under pressure in the $100-200^{\circ}$ C range. The procedure for carrying out the experiments was described in [5]. The catalysts used were Ca and La forms of zeolites of types A, X, and Y, erionite, mordenite, Li and K forms of Y type zeolite, and decationized forms of zeolites (Table 1). The degree of ion exchange was determined both from the residual Na⁺ and from the amount of cation introduced

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TABLE 1. Catalysts and Their Characteristics

Zeolite	SiO ₂ : Al ₂ O ₃	Degree of exchange, % (eq.)	Water content, %	Zeolite	SiO_2 : Al_2O_3	Degre e o f exchange % (eq.)	Water content, %
LiY KY MgY CaY LaY HY CaX LaX HX	5,0 5,0 5,0 5,0 5,0 5,0 2,9 2,9 2,9 2,9	73 70 76 85 .62 98 78 78 72 86	25,0 24,8 23,4 22,7 21,3 23,0 21,1 28,6 19,6	CaA LaA CaE LaE HE CaM LaM HM	2,0 2,0 6,0 6,0 10,0 10,0 10,0	92 58 86,6 52,9 69,6 69 54 93	24,4 23,4 20,2 21,8 19,0 11,5 12,6 14,3

TABLE 2. Activity of Zeolites in the Hydrogenation of Piperylene at 180°C

Ze olite	Yield of pen the presence	tenes, %, in of	Zeolite	Yield of pentenes, %, in the presence of	
	H ₂	He		H ₂	He
HX HY HE HM	31,4 10,6 14,0 0	5,9 2,7 3,9 1,5	LaX LaY CaX CaY	55,0 54,0 29,0 28,1	2,4 2,6 1,0 1,5

TABLE 3. Ratio of Reaction Products in the Hydrogenation of Piperylene on Ca and La Forms of Zeolites*

		Ca ²⁺	La ³⁺		
Z e olite	1-pentene 2-pentene	cis-2-pentene trans-2-pentene	1-pentene 2-pentene	cis-2-pentene trans-2-pentene	
A X Y E M	$0,56\pm0,06$ $0,63\pm0,08$ $0,69\pm0,07$ $0,79\pm0,13$ $0,96\pm0,25$	$\begin{matrix} 0,15\pm0,02\\ 0,33\pm0,06\\ 0,44\pm0,04\\ 0,41\pm0,07\\ 0,27\pm0,11 \end{matrix}$	$\begin{array}{c} 0,52{\pm}0,06\\ 0,43{\pm}0,11\\ 0,43{\pm}0,13\\ 0,51{\pm}0,08\\ 0,54{\pm}0,07\end{array}$	$\begin{array}{c} 0,38 {\pm} 0,06 \\ 0,34 {\pm} 0,14 \\ 0,37 {\pm} 0,11 \\ 0,40 {\pm} 0,09 \\ 0,33 {\pm} 0,05 \end{array}$	

*The standard deviations of the values of the ratios of the reaction products were calculated from 15-20 points.

TABLE 4. Relative Energy of Piperylene Conformers and Composition of Equilibrium Mixture at Various Temperatures

Piperylene	Relative	Content in mixture at the temperatures, "K		
conformer	mole	400	500	
syn-trans	2,28	0,04	0,06	
anti-trans	0,0	0,65	0,61	
syn-cis	18,41	0,0	0,0	
anti-cis		0,31	0,33	

into the zeolite. The concentrations of the Li⁺, Na⁺, and K⁺ cations were determined by flame photometry, and those of Ca^{2+} and La^{3+} were determined by titration with a solution of Trilon B.

DISCUSSION

The yield of hydrogenation products on the catalysts investigated usually decreased with time. Exceptions are the La forms of X and Y type zeolite, on which the yield remained unchanged over the course of the experiment (Fig. 1). The results of experiments according to a second analysis are given below. The H forms of the zeolites display a considerably



Fig. 1. Dependence of the yield of pentenes on the operating time of the catalyst: 1) LaY, 120°C; 2) LaX, 120°C; 3) CaX, 140°C; 4) CaY, 140°C.

Fig. 2. Dependence of the ionization potential on the electrostatic potential of cations of the main subgroups of groups I, II, and III in the periodic table.

lower activity in comparison to the cationic forms (Table 2). As we see from the data presented, at 180°C the yield of pentenes on the H forms of the zeolites varies from 0 to 30%, a certain portion of the products being formed as a result of the diproportionation of hydrogen, as shown by experiments carried out with the replacement of H_2 by He. The fact that the hydrogenating activity of the H forms of the zeolites is lower than that of their cationic forms has previously been noted in [6-8].

The results of the hydrogenation of piperylene on the Ca^{2+} and La^{3+} forms of the zeolites (Table 3) were obtained in experiments, in which the extent of conversion of piperylene varied from 5 to 50%. As we see from Table 3, the standard deviation is most often at the 10-15 rel. % level, i.e., the ratio of the reaction products is practically independent of the extent of conversion of piperylene. A similar finding was also noted in [5]. The constancy of the ratio of the yields of the reaction products over a broad range of extents of conversion of piperylene is evidence of the absence of secondary isomerization reactions involving olefins formed upon hydrogenation of the original hydrocarbon. The reason for this may be the difference between the adsorption capacities of the pentenes and piperylene on the zeolites.

As we see from Table 3, the 1-pentene/2-pentene ratio on the catalysts investigated is most often equal to 0.5, but on CaM it is 0.96 ± 0.25 . The cis-2-pentene/trans-2-pentene yield ratio is 0.2-0.4. The indicated values of the ratios basically coincide with those which were obtained on the Na forms of the zeolites in [5]. The ratio of the reaction products depends on whether the mechanism for the addition of hydrogen to the piperylene molecule includes the subsequent addition of individual atoms or whether the addition of molecular hydrogen occurs in one step [5]. The calculation of the ratios of the reaction products corresponding to either mechanism requires knowledge of the equilibrium composition of the syn and anti conformers of piperylene. For this purpose we carried out a quantum-chemical calculation of the relative energies of the piperylene conformers by the MO-LCAO-SCF method in the CNDO/2 approximation (Tables 1-4).

From Table 4 it follows that the equilibrium cis-piperylene/trans-piperylene ratio equals 0.45-0.48, which is close to the data in [9] and attests to the reliability of the results of the calculation.

The ratios of the reaction products for the atomic and molecular mechanisms for the hydrogenation of piperylene were calculated on the basis of the data in Table 4 according to the method described in [5] (Table 5). As in [5], the 1-pentene/2-pentene ratios equals 0.5 for the atomic mechanism and 1.0 for the molecular hydrogenation mechanism. The cis-

TABLE 5. Ratio of the Reaction Products for Different Mechanisms for the Hydrogenation of Piperylene

	Atomic hyd	rogenation	Molecular hydrogenation		
T, °K	1-pentene	cis-2-pentene	1-pentene	cis-2-pentene	
	2-pentene	trans-2-pentene	2-pentene	trans-2-pentene	
400 500	0,510 0,515	0,217 0,250	1,000 1,000	0,449 0,492	

TABLE 6. Dependence of the Specific Hydrogenating Activity of Y Type Zeolite on the Properties of Cations at 140°C

Cation	<i>I</i> , eV	e/r²	Activity, mole · 10 ⁴ g · h	Specific activity, <u>mole</u> · h
K +	4,34	0,56	0,718	0,022
Na+ *	5,14	1,04	1,435	0,044
Li +	5,39	2,16	0,718	0,022
Ca ²⁺	11,87	1,85	7,170	0,618
La ³⁺	19,17	2,00	53,100	9,020

*The data on the activity of NaY were taken from [5].

2-pentene/trans-2-pentene ratio equals 0.22-0.25 and 0.45-0.49, respectively, for the indicated hydrogenation mechanisms. These values differ from the previously obtained value 0.5, since in [5] different ratios of the syn and anti conformers in the equilibrium mixture were assumed. A comparison of the calculated 1-pentene/2-pentene ratios (see Table 5) with the experimental ratios (see Table 3) reveals that the occurrence of the reaction according to the atomic mechanism is more likely.

The experimental values of the cis-2-pentene/trans-2-pentene ratio (see Table 3) are between the values calculated for the atomic and molecular mechanisms for the hydrogenation of piperylene (see Table 5); however, they are most often closer to the values corresponding to the atomic mechanism. The absence of a better fit may be due to the deviation of the composition of the mixture of cis- and trans-piperylene on the catalyst surface from the equilibrium composition in the gaseous phase.

In [10] it was postulated that H_2 dissociates heterolytically when it is adsorbed on zeolites, the proton being bound to a lattice oxygen, and the hydride ion being bound to a metal cation. The hypothesis of the dissociative adsorption of H_2 in the case of hydrogenation on zeolites is consistent with the kinetics of the hydrogenation of 2-methyl-2-butene and the occurrence of the isomerization of the double bond during the hydrogenation of this hydrocarbon [11]. The results of the present investigation are also consistent with the hypothesis of the dissociative nature of H_2 .

The results of the quantum-chemical calculation of the adsorption of H_2 on zeolites [12] point out the fundamental possibility of the heterolytic dissociation of H_2 upon adsorption. In order to further refine the reaction mechanism, it is necessary to ascertain which hydrogen ion is added first to the unsaturated bonds of the compound being hydrogenated. For this purpose we performed a quantum-chemical calculation of the heats of reaction for the addition of a hydride ionfrom NaH and a proton from OH to a piperylene molecule.

The following values of the heats of reaction were obtained

$$\begin{array}{l} C_5H_8 + \operatorname{NaH} \rightarrow C_5H_9^- + \operatorname{Na^+} -42.3 \quad \text{kcal/mole} \\ C_5H_8 + \operatorname{OH} \rightarrow C_5H_9^+ + \operatorname{O^-} -58.6 \quad \text{kcal/mole} \end{array}$$

Thus, the addition of a hydride ion to C_5H_6 is a less endothermic process and is preferable. If the adsorption of the reactant molecules on zeolites is accompanied only by the deformation of the reacting bonds under the effects of the electrostatic field of the cations, the catalytic activity should be correlated with the value of the electrostatic potential of the









cations. If the adsorption is accompanied by more extensive interactions, which result in the transfer of an electron from the molecule to a cation, the activity will be determined by the electron affinity of the cations. The resolution of this question is hampered by the existence of a correlation between the high ionization potentials of the elements and the electrostatic potentials of the cations (Fig. 2).

As we see in Fig. 2, only Be deviates sharply from this dependence. In [6, 7] it was shown that the activity of zeolites in hydrogenation reactions passes through a maximum as a function of the value of the electrostatic potential of the cations. The location of Be on the descending branch of this dependence was attributed to the fact that the optimal energy of the bonding of the reacting molecules to the active sites of the catalyst was exceeded. Therefore, on the basis of the data previously obtained it was not possible to determine which property of the cations governs the hydrogenating activity. Among the cations of groups I, II, and III in the periodic table we can select some, for which one of the properties varies while the other remains approximately constant. As we see from Table 6, the ionization potential of the element varies by no more than 20% in the series K⁺, Na⁺, Li⁺, but the electrostatic potential of the cations varies by a factor of 4. In the case of Li⁺, Ca²⁺, La³⁺, on the other hand, the ionization potential varies by a factor of 4, and the electrostatic potential is constant to within 10%.

In the calculation of the specific activities of the cations (see Table 6) we took into account only the cations which are located in the large cages in zeolite Y, and for the singly charged cations we assumed that only 75% of them are located in the large cages (40 of the 56 cations in the unit cell for zeolite Y with the ratio $SiO_2/Al_2O_3 = 5.0$). In the case of the multiply charged Ca^{2+} and La^{3+} cations, for which the number of cations is smaller than the number of sites for them in the zeolite, the method described in [13] was used to determine the distribution of the cations among the accessible and inaccessible sites in the zeolite. For this purpose the zeolite was decationized at $\sim 20^{\circ}$ C by an excess of an NH₄Cl solution, and the number of cations entering the solution, as well as the number remaining in the zeolite, were determined by chemical analysis. In zeolite CaY 60.9% of the Ca²⁺ cations are located in large cages, since they are easily exchanged for NH₄⁺ at $\sim 20^{\circ}$ C, and 35% of the cations are located in the cubic octahedrons and hexagonal prisms. The absence of complete balance is apparently due to the insufficient accuracy of the analysis.

In the case of zeolite LaY, the distribution of the cations among the large cages and hexagonal prisms is 69.9 and 25.1%, respectively. As we see from the data in Table 6, the specific activity of the cations is determined by the value of the highest ionization potential of the element and does not depend on the electrostatic potential of the cation. At the same time, there is an exponential dependence of the activity on the ionization potential (Fig. 3). This is attributed to the decrease in the apparent activation energy of the reaction (Fig. 4).

CONCLUSIONS

1. The 1-pentene/2-pentene and cis-2-pentene/trans-2-pentene ratios in the reaction products of the hydrogenation of piperylene on the Ca^{2+} and La^{3+} forms of various zeolites are close to the values characteristic of the successive addition of hydrogen ions to unsaturated bonds. As the quantum-chemical calculation of the heats of reaction has shown, a hydride ion is added to the piperylene molecule first.

2. The hydrogenating activity of zeolites is determined by the electron affinity of the metal cation.

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