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Abstract

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P. N. GALICH, A. A. GUTYRYA, Corresponding Member of the Academy of Sciences of the USSR V. S. GUTYRYA, and I. E. NEIMARK

ON SOME FEATURES OF THE CATALYSIS OF ALKANES ON ZEOLITES (MOLECULAR SIEVES)

In recent years, the interest of many researchers in studying the adsorption properties of zeolites has been aroused chiefly by the specificity of adsorption selectivity on these sorbents, which made it possible to introduce the concept of a zeolite as a "molecular sieve" (1). Considering, however, the closeness of zeolites in chemical composition and adsorption characteristics to the group of natural and synthetic aluminosilicate catalysts, it seemed important also to evaluate the catalytic properties of "molecular sieves." At the same time, it could be assumed *a priori* that there would be a considerable effect of "deformation" of the catalysis mechanism, due both to the increased selectivity of adsorption of molecules (selection according to the dimensions of the effective cross section) of the initial substance, and to the possible inhibition of reactions leading to the formation of large branched or cyclic systems whose dimensions do not correspond to the dimensions of the adsorbing cavities of the zeolite. Naturally, such an effect should be observed in the micropores of any adsorbent used in one or another act of catalysis; however, by virtue of the uniformity of their structure and pore sizes, zeolites make it possible to isolate the spatial effect of catalysis from the general background of reactions proceeding in large pores.

A preliminary study of the dehydrogenation reaction of alkanes having 6 or more carbon atoms in the linear chain on zeolites of the CaA form made it possible to observe the smooth dehydrogenation of *n*-alkanes to linear olefins without accompanying skeletal isomerization and cyclization, as occurs on typical aluminosilicate and aluminochromium catalysts.

Further study of the dehydrogenation catalysis of *n*-alkanes on molecular sieves allowed us to clarify the mechanism of this phenomenon and to characterize the external effect of the catalysis of *n*-alkanes on zeolites as a "pseudo-effect." The latter is due not to steric hindrance for intracavity dehydrocyclization and skeletal isomerization, but to the absence of the possibility for the complex molecules formed to pass from the zones of the internal cavities into the external zones through channels of smaller cross section, in accordance with existing ideas about the structure of zeolites (1). Thus, for the process of desorption of

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

catalysis products we have the same effect of "molecular sieving" on zeolites as selective sorption on them in processes of separating mixtures of substances with different effective molecular cross sections. The experimental material set forth below, the analytical treatment of which enabled us to observe and describe the pseudocatalytic effect of dehydrogenation of *n*-alkanes on zeolites of the CaA form, is presented below.

The present communication describes the kinetic regularities of the reactions proceeding during the cracking of *n*-dodecane on CaA zeolite, as well as the nature of the products formed. As the object of investigation, a sample of tableted zeolite (molecular sieve) of the CaA type was taken.

From Fig. 1, which presents the sorption isotherms of water, hexane, and benzene vapors, it is evident that the zeolite sample taken as the catalyst possessed sharply selective adsorption properties for molecules of different configuration and size.

The windows of the elementary cavities of the crystalline structure of this zeolite are accessible to water molecules and normal paraffins, but are not accessible to benzene molecules, whose critical size exceeds 5 Å. Water and hexane vapors are well adsorbed on CaA zeolite; benzene is practically not sorbed. The limiting sorption capacity of the zeolite with respect to $C_{12}H_{26}$ at 250 was 0.386 mM/g. On the molecular-sieve sample used,

Fig. 1. Sorption isotherm of water vapors (I), hexane (II), and benzene (III) on CaA zeolite

Fig. 2. Kinetics of cracking of *n*-dodecane at different temperatures:
1 –525°, $\beta = 1.02$;
2 –500°, $\beta = 1.0$;
3 –475°, $\beta = 1.0$;
4 –450°, $\beta = 1.0$

chromatographic separation of a standard mixture–hydrogen, methane, carbon monoxide–proceeds well. The feed was *n*-dodecane (b.p. = 215.3-216.5°, d_4^{20} 0.7490, n_D^{20} 1.4218). The experiments were carried out in the apparatus described earlier (1).

The experimental data are given in Table 1. The condensate was distilled on a rectification column with 15 theoretical plates. The fractions obtained were studied by spectral methods. The results of this study are presented in Table 2.

The data presented show that, as a result of the cracking of *n*-dodecane on CaO zeolite, cyclic compounds are absent from the reaction products. Decomposition of *n*-dodecane occurs mainly in the middle of the molecule, as indicated by the maximum content of hexenes in the condensate. Migration of the double bond to the middle of the carbon chain without transformation of the hydrocarbon skeleton also takes place, as is evident from the predominant content of β-olefins.

As a result of processing the data presented, it was established that the cracking of n-dodecane on zeolite obeys the Frost equation (2), describing the kinetics of heterogeneous-catalytic reactions inhibited by reaction products (Fig. 2). The found value of the activation energy is $A = 35{,}100$ kcal/mol. To determine the nature of coke-like products, the spent molecular sieves, after decomposition with 0.1 N HCl solution, were extracted with sulfuric ether.

Table 1

Properties of the products of cracking of n-dodecane

Parameters	450° 0.3	450° 0.5	450° 1.0	475° 0.3	475° 0.5	475° 1.0	500° 0.3	500° 0.5	500° 1.0	525° 0.3	525° 0.5	525° 1.0
Space velocity, h^{-1}												
Catalyst yield, wt. %	89.0	92.8	94.0	75.5	86.0	91.1	59.2	69.7	83.2	42.5	52.6	69.8
NK-100° fraction (on catalyst)	11.4	8.3	4.5	18.4	14.2	11.5	24.6	19.7	15.0	26.6	23.8	19.5
Bromine number of the catalyst	12.9	9.6	3.2	22.0	18.3	11.9	33.4	28.0	19.7	29.2	25.2	24.0
Gas yield, wt. %	4.9	1.3	0.4	13.2	7.3	3.0	28.5	19.7	8.4	41.4	36.2	20.3

Parameters	450° 0.3	450° 0.5	450° 1.0	475° 0.3	475° 0.5	475° 1.0	500° 0.3	500° 0.5	500° 1.0	525° 0.3	525° 0.5	525° 1.0
Coke, wt. %	3.1	2.8	2.7	5.8	4.0	3.4	7.3	6.0	53	10.9	8.0	6.9
Losses	3.0	3.1	2.8	5.5	2.7	3.8	5.0	4.6	3.1	5.2	3.2	3.0
Gas composition, wt. %												
Hydrogen	—	—	—	5.74	2.58	8.66	10.9	7.99	8.35	16.20	8.92	8.61
Ethylene	—	—	—	9.57	9.79	9.75	9.96	9.93	13.21	10.00	10.04	12.23
n-Butylene + propylene	—	—	—	29.60	30.46	29.1	29.28	28.77	27.84	27.60	27.62	28.99
Isobutylene	—	—	—	—	—	—	—	—	—	—	—	—
$C_{nH_{2n+2}}$	—	—	—	54.21	57.23	52.07	49.7	53.3	50.6	46.7	53.45	50.17

Table 2

Composition of the fraction from catalysis of *n*-dodecane, obtained at 500° and a space velocity of 0.5 h^{-1}

Fraction No.	T, °C	Hydrocarbons detected	Established from bands, cm^{-1}	Note
I	35.5–36.5	trans-2-pentene cis-2-pentene	1765, 1711, 1655, 1243, 978, 816, 715, etc. 1650, 1466, 964, 922, etc.	The trans form predominated
II	36.5–63.5	was not analyzed because of its small amount		

Fraction No.	T, °C	Hydrocarbons detected	Established from bands, cm^{-1}	Note
III	63.5—68	trans-2-hexenecis-2-hexenehexene-1trans-hexene-1 cis-hexene-1	1822, 1799, 1725, 1066, 968, 842, etc.1658, 1453, 1641, 1463, 1414, 9229111649, 1444, 1301, 1668, 889, 1301, 1254, etc.	Small amountsAccording to combination-scattering spectra
IV	68—94	trans-hexene-1heptene-1	1821, 1780, 1725, 981, 780, 755, etc.723, 835, 908, 1002, 1647, etc.	Small amounts
V	94—108	cis- and trans-heptene-2heptene-16-methyl-heptene-1	1658, 1468, 1460, 1345, 1032, 1103, 933925, 992, 1646, 1043, 1085, 1110, etc.	Traces, according to combination-scattering spectra

The extraction product was a mobile liquid of dark-brown color. The iodine number, determined by Hübl' s method, was 115, and the molecular weight 112. After hydrogenation in a hexane solution in an autoclave over Raney nickel at 50° and a pressure of 130 atm, the hydrogenate was separated by chromatography on silica gel. Two fractions were obtained—dearomatized, with n_D^{20}1.4235, and aromatized, with n_D^{20}1.5152. By spectral methods it was possible to establish a chain containing more than four carbon atoms with branching (bands 1464, 1461, 722, 1377 cm^{-1}).

The second fraction consisted of aromatic structures, mainly mono-, di-, and trisubstituted benzenes (bands 1607, 1480, 1450 cm^{-1}). Analysis in the ultraviolet region showed the presence of substances containing a naphthalene ring.

The results obtained show that in the cavities of molecular sieves there occur both dehydrocyclization reactions with the formation of aromatic hydrocarbons and isomerization reactions; however, owing to the limited dimensions of the outlet apertures (“windows”), the hydrocarbons formed cannot leave the zeolite cavities, being a source of the formation of condensation products and coke. Thus, under cracking conditions on CaA zeolite, the phenomenon of a "pseudo-effect" of noncyclic dehydrogenation of *n*-alkanes is observed.

Institute of Chemistry of Polymers and Monomers
Academy of Sciences of the Ukrainian SSR

Institute of Physical Chemistry
Academy of Sciences of the Ukrainian SSR

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